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A TREATISE ON CHEMISTRY

"*Chymia, alias, Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723

John Dalton.

Engraved by C. H. Jeens from a Daguerreotype

London: Published by Macmillan & Co.

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A
TREATISE ON CHEMISTRY

BY

SIR H. E. ROSCOE, F.R.S. AND C. SCHORLEMMER, F.R.S.

VOLUME I

THE NON-METALLIC ELEMENTS

NEW EDITION COMPLETELY REVISED BY SIR H. E. ROSCOE ASSISTED
BY DRS. H. G. COLMAN AND A. HARDEN, WITH TWO HUNDRED
AND SEVENTEEN ILLUSTRATIONS, AND A PORTRAIT OF
DALTON ENGRAVED BY C. H. JEENS

London
MACMILLAN AND CO., LIMITED
NEW YORK: THE MACMILLAN COMPANY
1905

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Second Edition, 1894
Third Edition, 1905

PREFACE TO THE FIRST EDITION

It has been the aim of the authors, in writing the present treatise, to place before the reader a fairly complete, and yet a clear and succinct statement of the facts of Modern Chemistry, whilst at the same time entering so far into a discussion of Chemical Theory as the size of the work and the present transition state of the science permit. Special attention has been paid to the accurate description of the more important processes in technical chemistry, and to the careful representation of the most approved forms of apparatus employed. As an instance of this, the authors may refer to the chapter on the Manufacture of Sulphuric Acid. For valuable information on these points they are indebted to many friends both in this country and on the Continent.

The volume commences with a short historical sketch of the rise and progress of chemical science, and a few words relative to the history of each element and its more important compounds preface the systematic discussion of their chemical properties. For this portion of their work, the authors wish here to acknowledge their indebtedness to Hermann Kopp's classical works on the History of Chemistry.

In the part of the volume devoted to the description of the non-metallic elements, care has been taken to select the most recent and exact experimental data, and to give references in all important instances, as it is mainly by consulting the original memoirs that a student can obtain a full grasp of his subject.

Much attention has likewise been given to the representation of apparatus adapted for lecture-room experiment, and the numerous new illustrations required for this purpose have all been taken from photographs of apparatus actually in use. The fine portrait which adorns the title-page is a copy, by the skilful hands of Mr. Jeens, of a daguerreotype taken shortly before Dalton's death.

MANCHESTER, *July*, 1877.

PREFACE TO THE SECOND EDITION

IN this new, completely revised and reprinted edition I have endeavoured to carry out the aims which were put forward in the preceding preface seventeen years ago. Deprived of the aid of my late friend and colleague, I have been fortunate in securing the help of two of the ablest of my former students, and to them I tender my thanks. How far we have succeeded in bringing this edition up to the level of the science of the present day, it will be for the public to judge. All I can say is that no pains have been spared to do so.

H. E. ROSCOE.

LONDON, *September 29th*, 1894.

PREFACE TO THE THIRD EDITION

THE ever-increasing progress which Chemistry in all its branches is making demands a frequent revision of all text-books. I am glad again to have to thank my friends, Drs. Colman and Harden, for the able assistance which they have given me; indeed, to them belongs the whole credit of bringing this edition up to date.

I have also to express my obligations to Messrs. Walter King, George Lunge, George Matthey, M. W. Travers, and T. E. Thorpe for permission to use illustrations, and to thank Mr. W. J. Young, M.Sc., for assistance.

H. E. ROSCOE.

April, 1905.

CONTENTS

CONTRACTIONS EMPLOYED IN THIS VOLUME

ABBREVIATED TITLE	JOURNAL
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Arch. Néerland.	Archives Néerlandaises des Sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Chem. Centr.	Chemisches Centralblatt.
Chem. News	Chemical News.
Chem. Zeit.	Chemiker Zeitung.
Compt. Rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).

ABBREVIATED TITLE	JOURNAL
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Path. Soc.	Transactions of the Pathological Society.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

CHEMISTRY

CHEMISTRY

HISTORICAL INTRODUCTION

In looking back at the history of our Science, we find that although the ancient world possessed a certain empirical knowledge of chemical facts derived chiefly from an acquaintance with pharmaceutical and manufacturing art, the power of connecting or systematising these facts was altogether wanting.

The idea of experimental investigation was scarcely understood, and most of those amongst the ancients who desired to promote a knowledge of Nature attempted to do so rather by pursuing the treacherous paths of speculation, than the safe though tedious route of observation and experiment. They had no idea of the essential differences which we now perceive between elements and compound substances, nor did they understand the meaning of chemical combination. The so-called Aristotelian doctrine of the four elements, Earth, Water, Air or Steam, and Fire, bore no analogy to our present views as to the nature and properties of the chemical elements, for with Aristotle these names rather implied certain characteristic and fundamental properties of matter than the ideas which we now express by the term chemical composition. Thus "Earth" implied the properties of dryness and coldness; "Water," those of coldness and wetness; "Air or Steam," wetness and heat; "Fire," dryness and heat. All matter was supposed to be of one kind, the variety which we observe being accounted for by the greater or less abundance of these four conditions which were supposed to be essential to every substance, that which was present in the greatest degree giving to the substance its characteristic properties. To men holding such views, a change of one kind of matter into a totally different kind appeared probable and natural. Thus, the formation of water from air or *vice versâ* is described by Pliny as a usual phenomenon seen in the formation and disappearance of clouds, whilst the ordinary experience that cold acts as a solidifying and hardening agent bears out Pliny's view, that rock crystal is produced from moisture, not by the action of heat, but by that of cold, so that it is, in fact, a kind of ice. A transformation of one sort of substance into another quite different thus appears not only possible but probable, and we are not surprised to learn that, under the influence of the Aristotelian philosophy, which throughout the middle ages was acknowledged to be the highest expression of scientific truth, the question of the transmutability of the base into the noble metals was considered to be a perfectly open one.

Much light of a very interesting and remarkable character has been thrown upon the origin of alchemy, the artificial production of the noble metals, by the discovery of an Egyptian papyrus, which contains more than a hundred metallurgical recipes written in Greek, many of which consist of elaborate directions for the falsification of the precious metals. The connection between these working notes of a fraudulent Egyptian goldsmith and the dreams of the later alchemists is attested by the reappearance of several of these very recipes in the writings of the following century under the guise of formulæ of transmutation.[1]

The oldest works of a strictly chemical character date from about the beginning of the third century of our era, and are due to Greek authors resident in Egypt, where our science appears to have had its birth. These early workers were familiar with the processes of distillation, sublimation, and digestion, and their writings are illustrated by rough drawings of the apparatus employed for these purposes. Among these writers, the most ancient and distinguished of whom is known as Zosimus of Panopolis, the possibility of the transmutation of the metals is fully accepted, and their works consist mainly of directions for the achievement of this object, couched however in language so deeply tinged with religious mysticism, symbolism, and metaphor as to be almost unintelligible.[2] They allude to their subject as

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[1] Berthelot, *Les Origines de l'Alchimie*, p. 3. *Introduction à l'Etude de la Chimie des Anciens et du Moyen Age*, pp. 21, 59.

[2] Berthelot, *Collection des Anciens Alchimistes Grecs.* Part I.

the "divine art," and it is not until the fourth century that we find in the works of the Byzantine writers the term *Chemia* applied to the art which treats of the production of gold and silver.[1] The fact that all these authors were closely connected with the celebrated schools of Alexandria, the last resting-place of the proscribed secrets of the Egyptian priests, adds to the probability that our science was first extensively practised in Egypt, although there are indications of early Babylonian and Chaldean traditions, and alchemical ideas also appear to have arisen and to have been developed independently in India.[2] Plutarch, indeed, states that the old name for Egypt was *Chemia*, and that this name was given to it on account of the black colour of its soil. The same word was used to designate the black of the eye, as the symbol of the dark and mysterious. It is therefore possible that chemistry originally meant simply the Egyptian—or secret—knowledge, whilst others identify the name with the Greek χυμός, sap or liquid, the name of the agent of transmutation being applied to the art.

The Aristotelian philosophy and the Greek alchemy became known to the Arabians in Persia (about 640 A.D.) through the medium of the Syriac translations made by the philosophers who had fled thither from the ancient schools of Egypt and Syria, closed by the decrees of the Byzantine emperors.[3] It seems probable that the Arabs also became acquainted with Hindu science in Persia, and thus united the learning of the East and West. The Arabs carried the science back through Egypt, and thence through Northern Africa into Spain, and by them the Arabic article was affixed to the original name, so that the word *Alchemy* has from that time been used to signify the art of making gold and silver.

The Arabs made but little progress and concealed their doctrines in the vague, mystical, semi-religious language of the Greeks. Among them, however, grew up the first beginnings of a chemical theory (Avicenna) which gradually became more precise and was universally acknowledged later on in the twelfth century. This asserts that the essential differences between the metals are due to the preponderance of one of two principles —mercury and sulphur—of which all the metals are composed.

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[1] Kopp, *Beiträge zur Geschichte der Chemie.* 1 Stück, p. 40.

[2] P. C. Rây, *History of Hindu Chemistry.* Vol. I. (Williams & Norgate, 1902).

[3] Berthelot, *La Chimie au Moyen Age* (*Paris*, 1893).

The first principle is characteristic of the truly metallic qualities, whilst the latter causes the peculiar changes noticed when the metals are exposed to heat. The noble metals are supposed to contain a very pure mercury, and are, therefore, unalterable by heat, whilst the base metals contain so much sulphur that they lose their metallic qualities in the fire. These constituents may, however, not only be present in different proportions, but also in different degrees of purity or in different states of division; and thus it might naturally be supposed that, if not by a variation in their relative quantity, at any rate by a change in their condition, such an alteration in the properties of one metal might be brought about as would produce from it some other known metal. Thus gold and silver contain a very pure mercury, which in the one instance is combined with a red and in the other with a white sulphur; further, the reason why these two metals amalgamate so easily is that they already contain a large quantity of mercury, and are therefore quickly attracted by the liquid metal.

Whilst Greece and Italy sank deeper and deeper into barbarism, arts and science flourished under Arabian dominion, and the academies of Spain were thronged with students from all parts of the Christian world. The knowledge of alchemy spread from this source over Western Europe, and in the thirteenth century we find alchemists of the Arabian school in all the chief countries of Europe. In France we hear of Arnold Villanovanus and Vincent of Beauvais; Albertus Magnus flourished in Germany; our own Roger Bacon (1214-1294) was also an alchemist, and was tried at Oxford for sorcery, and, to disprove these charges, wrote the celebrated treatise[1] in which he shows that appearances then attributed to supernatural agency were due to common and natural causes. It was Roger Bacon, from his rare accomplishments and learning termed Doctor Mirabilis, who first pointed out the possible distinction between theoretical alchemy, or chemistry studied for its own sake, on the one hand, and practical alchemy, or the striving after certain immediately useful ends, on the other.

Alchemical writings were also at this time falsely attributed by their anonymous authors to the great names of Raymond Lully, Thomas Aquinas, and many others.

To the thirteenth century also belong the Latin works which purport to be translations of the Arabian writings of Geber or

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[1] *Epistola de secretis operibus artis et naturæ, et nullitate magiæ.*

Djaber, but which bear no resemblance in form or contents to the genuine works of this alchemist.[1]

This Latin writer describes various chemical operations, such as filtration, distillation, crystallisation, and sublimation, many of which had been known from the time of the Greeks; and by these he prepares new substances or purifies the old ones. Bodies such as alum, green vitriol, saltpetre, and sal-ammoniac are employed; and we find that he was able to prepare nitric acid, or *aqua fortis*, and from it the valuable solvent for gold, *aqua regia.* It is probable that even sulphuric acid was known to him, and he was certainly acquainted with a number of metallic compounds, amongst which were mercuric oxide and corrosive sublimate, the preparation of which he describes.

Although all these men agreed that the transmutation of metals was not only possible but that it was an acknowledged fact, and that for the preparation of gold and silver the philosopher's stone was needed, it is difficult, not to say impossible, now to understand their methods or processes, inasmuch as all that they have written on this subject is expressed in the ambiguous and inflated diction of the Byzantine and Arabian authors.

The fourteenth century finds the study of alchemy widely spread over the civilised world, and the general attention which the subject attracted gave rise to the discovery of a large number of chemical substances. By the end of the fifteenth century, although the knowledge of chemical facts had continued to increase, the old views respecting the ultimate composition of matter were still accepted. In addition, however, to the sulphur and mercury, supposed to be the universal constituents of matter, we find a third constituent, viz., salt, introduced. We must bear in mind however that these three principles, like the four Aristotelian elements, were not supposed to be identical with the common substances which bear their names.

That men of such wide experience and great powers, as the chemists of this period proved themselves to be, could bring themselves to believe in the possibility of the discovery of the philosopher's stone, a substance of such potency that when thrown on the base metals in a state of fusion (moment of projection) it transmutes them into gold and silver, appears to us very remarkable. No one doubted the possibility of such a transmutation, and the explanation may be found in the fact,

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[1] Berthelot, *La Chimie du Moyen Age.* Vol. III.

at that time well known, that the colour of certain metals can be altered by the addition of other bodies. Thus the Latin Geber knew that when red copper is melted with tutty (an impure oxide of zinc), the golden-yellow brass is obtained; and also that other minerals (those which we now know to contain arsenic) give to copper a silver-white colour. Still, the difference between these alloys and the noble metals must soon have been discovered, and the possibility of the transmutation lay rather in the notion already alluded to, that the different metals contained the same constituents arranged either in different quantities or in different states of purity. Nor were experimental proofs of this view wanting. Thus Geber believed that by adding mercury to lead the metal tin was formed, and the solid amalgam does closely resemble tin in its appearance. Then again the metallurgical processes were in those days very imperfect, and the alchemists saw proof of their theory in the formation of a bead of pure silver from a mass of galena, or in the extraction of a few grains of gold out of a quantity of pyrites. It was not until the beginning of the seventeenth century that it was proved that galena frequently contains silver, and that traces of gold are often found in iron pyrites. Even so late as 1709 we find Homberg stating that pure silver after melting with pyrites is found to contain gold, and it was only after several chemists had performed the experiment with a like result that the mineral itself was acknowledged to contain traces of gold.

Again, it was not at this time recognised that some salts are metallic compounds, and the precipitation of copper from a solution of blue-stone by metallic iron was supposed to be a transmutation of iron into copper. These apparent experimental proofs of the truth of the alchemical doctrine were accompanied by a mass of traditional evidence; that is, of stories handed down from generation to generation, in which cases of the transmutation of metals are circumstantially narrated. Thus the belief in the fundamental principle of alchemy became firmly established.[1]

A satisfactory explanation of the belief in the power of the philosopher's stone to heal disease and to act as the *elixir vitæ*, the grand panacea for human ills, is more difficult to find. It

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[1] For further information on this subject Kopp's classical works, *Die Geschichte der Chemie*, and *Die Alchemie*, Thomson's *History of Chemistry*, and the various works of Berthelot, already quoted, may be consulted.

may possibly have at first arisen from a too literal interpretation of the oriental imagery found in the early Arabian writers, where, although the peculiar doctrine of *elixir vitæ* is unknown, we find such passages as the following:—"If thou carriest out my prescription with due care thou shalt heal the bad disease of poverty." The Arabians called the base metals "diseased." Thus Geber says, "Bring me the six lepers, so that I may heal them;"—that is, transmute the other six known metals into gold. The belief in the healing power of the philosopher's stone was also much strengthened by the discovery, about this time, of many substances which produce remarkable effects on the human frame, and of these the alchemists of the thirteenth century write in the most exaggerated and exalted terms.

The work known by the fantastic title of the *Triumph-Wagen des Antimonii*, which contains a large amount of accurate information concerning the preparation and the medicinal properties of many of the compounds of antimony, and is ascribed to the authorship of a monk, Basil Valentine by name, who was supposed to have lived at the beginning of the fifteenth century, has been shown by the late Prof. Schorlemmer to be an undoubted forgery dating from about 1600, the information being culled from the works of other writers and thrown into the mystical, semi-religious style suitable to the earlier period.[1] The same appears to be true of the other writings attributed to this author.

The man who effected the inestimable union between chemistry and medicine was Paracelsus (1493-1541). He not only assumed the existence of three components of all inorganic substances, but he was the first who included animal and vegetable bodies in the same classification, and held that the health of the organism depends on the continuance of the true proportions between these ingredients, whilst disease is due to a disturbance of this proper relation.

The era thus inaugurated by Paracelsus continued up to the end of the seventeenth century. Chemistry was the handmaid of medicine, and questions respecting the ultimate composition of matter were considered of secondary importance to those relating to the preparation of drugs. Of the contemporaries of Paracelsus, Agricola (1490-1555) was one of the most distinguished, and his remarkable work *De Re Metallica* contains a complete treatise on metallurgy and mining, which did much

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[1] See also Kopp, *Beiträge* III. 110.

to advance the processes of technical chemistry, many of the methods which he describes being in use even at the present day. Whilst Agricola devoted himself to the study of metallurgy, his countryman Libavius greatly assisted the general progress of science, inasmuch as he collected together, in writings which are characterised by a clear and vigorous style, all the main facts of chemistry; so that his *Alchemia*, published in 1595, may be regarded as the first handbook of chemistry. His chief object was the preparation of medicines, but he still maintained the science in its old direction and distinctly believed in the transmutation of metals.

The first who formally declined to accept the Aristotelian doctrine of the four elements, or that of Paracelsus of the three constituents of matter, was Van Helmont (1577-1644). He denied that fire has any material existence, or that earth can be considered as an element, for it can, he says, be produced from water, but he admitted the elementary nature of air and water, and gave great prominence to the latter in its general distribution throughout animate and inanimate nature. Van Helmont's acknowledgment of air as an element is the more remarkable, as he was the first to recognise the existence of different kinds of air and to use the term gas. Thus, his "gas sylvestre," which he clearly distinguished from common air, is carbonic acid gas, for he states that it is given off in the process of fermentation, and also formed during combustion, and that it is found in the "Grotto del Cane," near Naples. He also mentions a "gas pingue" which is evolved from dung, and is inflammable. It was Van Helmont who first showed that if a metal be dissolved in an acid it is not destroyed, as was formerly believed, but can again be obtained from solution as metal by suitable means; and he considered the highest aim of the science to be the discovery of a general solvent which would at the same time serve as a universal medicine, and to which the name of "alkahest" was given.

Although Van Helmont accomplished much towards the overthrow of the Paracelsian doctrine, his discoveries of the different gases were forgotten, and even up to the middle of the seventeenth century much divergence in opinion on fundamental questions prevailed. Those who were interested in the connection of chemistry with medicine still believed in the dreams of the alchemist, and held to the old opinions; whilst those who, advancing with the times, sought to further the science for its own sake, or for the sake of its important technical applications, often upheld views more in accordance with those which we now know to be the true ones. Among the names of the men who, during this period, laboured successfully to promote the knowledge of chemistry, that of Glauber (1603-1668) must be first mentioned. He was both alchemist and medicinal chemist, and discovered many valuable medicines. Another name of importance at this epoch is that of N. Lemery (1645-1715). He, as well as Lefebre and Willis, believed in the existence of five elements: mercury or spirit, sulphur or oil, and salt are the active principles; water or phlegm, and earth are the passive ones. Lemery's ideas and teachings became well known through the publication of his *Cours de Chymie* (1675), which was translated into Latin, as also into most modern languages, and exerted a great influence on the progress of the science. In this work the distinction between mineral and vegetable bodies was first clearly pointed out, and thus for the first time the distinction between Inorganic and Organic chemistry was realised.

Pre-eminent amongst the far-seeing philosophers of his time stands Robert Boyle (1627-1691). It is to Boyle that we owe the complete overthrow of the Aristotelian as well as the Paracelsian doctrine of the elements, so that, with him, we begin a new chapter in the history of our science. In his *Sceptical Chymist*[1] he upholds the view that it is not possible, as had hitherto been supposed, to state at once the exact number of the elements; that on the contrary all bodies are to be considered as elements which are themselves not capable of further separation, but which can be obtained from a combined body, and out of which the compound can be again prepared. Thus he states, "That it may as yet be doubted whether or no there be any determinate number of elements; or, if you please, whether or no all compound bodies do consist of the same number of elementary ingredients or material principles."[2] Boyle, it is clear, was the first to grasp the idea of the distinction between an elementary and a compound body, the latter being a more complicated substance produced by the union of two or more simple bodies and differing altogether from these in its properties. He also held that chemical

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[1] *The Sceptical Chymist or Chymico-physical Doubts and Paradoxes, touching the Experiments whereby vulgar Spagyrists are wont to endeavour to evince their Salt, Sulphur, Mercury, to be the true Principles of Things. First published in* 1661 (Boyle's Works, 1772, **1**, 458).

[2] Boyle's Works, 1772, **1**, 560.

combination consists in an approximation of the smallest particle of matter, and that a decomposition takes place when a third body is present, capable of exerting on the particles of the one element a greater attraction than the particles of the other element with which it is combined. More, however, than for his views on the nature of the elements, is science indebted to Boyle for his clear statement of the value of scientific investigation for its own sake, altogether independent of any application for the purposes either of the alchemist or of the physician. It was Boyle who first felt and taught that chemistry was not to be the handmaid of any art or profession, but that it formed an essential part of the great study of Nature, and who showed that from this independent point of view alone could the science attain to vigorous growth. He was, in fact, the first true scientific chemist, and with him we may date the commencement of a new era for our science, when the highest aim of chemical research was acknowledged to be that which it is still upheld to be, viz., the simple advancement of natural knowledge.

In special directions Boyle did much to advance chemical science (his published writings and experiments fill six thick quarto volumes), particularly in the border land of chemistry and physics; thus in the investigations on the "Spring of the Air," he discovered the great law of the relation existing between volumes of gases and the pressures to which they are subjected, which still bears his name.

Although Boyle was aware of the fact, which had long been known, that many metals when heated in the air form calces which weigh more than the metals themselves, and although he examined the subject experimentally with great care, his mind was so much biassed by the views he held respecting the material nature of flame and fire that he ignored the true explanation of the increase of weight, namely, that it is due to the absorption of a ponderable constituent of the atmosphere, and looked upon the gain as a proof of the ponderable nature of fire and flame, giving many experiments having for their object the "arresting and weighing of igneous corpuscles." [1]

Similar views are found expressed in his essay "On the Mechanical Origin and Production of Fixedness,"[2] written in 1675, where Boyle, speaking of the formation of mercuric oxide from the metal by exposure to the air at a high temperature, says, "chemists and physicians who agree in supposing this pre-

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[1] Boyle's Works, **3**, 706—718.

[2] Boyle's Works, **4**, 309.

cipitate to be made without any additament, will, perchance, scarce be able to give a more likely account of the consistency and degree of fixity, that is obtained in the mercury: in which, since no body is added to it, there appears not to be wrought any but a mechanical change, though I confess I have not been without suspicions that in philosophical strictness this precipitate may not be made *per se*, but that some penetrating igneous particles, especially saline, may have associated themselves with the mercurial corpuscles."

We owe the next advances in chemistry to the remarkable views and experiments of Hooke (*Micrographia*, 1665), and of John Mayow (*Opera Omnia Medico-physica*, 1681). The former announced a theory of combustion, which, although it attracted but little notice, more nearly approached the true explanation than many of the subsequent attempts. He pointed out the similarity of the actions produced by air and by nitre or saltpetre, and he concluded that combustion is affected by that constituent of the air which is fixed or combined in the nitre.[1] Hooke did not complete his theory or give the detail of his experiments, but similar conclusions seem to have been independently arrived at by Mayow, who in 1669 published a paper, *De Sal-Nitro et Spiritu Nitro-aëreo*, in which he points out that combustion is carried on by means of this "spiritus nitro-aereus" (another, and not an inappropriate name for what we now call oxygen), and he also distinctly states that when metals are calcined, the increase of weight observed is due to the combination of the metal with this "spiritus." Mayow was one of the first to describe experiments made with gases collected over water, in which he showed that air is diminished in bulk by combustion, and that the respiration of animals produces the same effect. He proved that it is the nitre-air which is absorbed in both these processes, and that an inactive gas remains, and he drew the conclusion that respiration and combustion are strictly analogous phenomena. There is, therefore, no doubt that Mayow clearly demonstrated the heterogeneous nature of air, although his conclusions were not admitted by his contemporaries.

Another theory which was destined greatly to influence and benefit chemical discovery, was advanced about this time by J. J. Becher (1635—1682), and subsequently much developed and altered by G. E. Stahl (1660—1734). It made special reference to the alterability of bodies by fire, and to the

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[1] *Micrographia*, pp. 103—5.

explanation of the facts of combustion. Becher assumed that all combustible bodies are compounds, so that they must contain at least two constituents, one of which escapes during combustion, whilst the other remains behind. Thus when metals are calcined, an earthy residue or a metallic calx remains; metals are therefore compounds of this calx with a combustible principle, whilst sulphur and phosphorus are compounds containing a principle which causes their combustion. Bodies unalterable by fire are considered to have already undergone combustion; to this class of bodies quicklime was supposed to belong, and it was assumed that if the substance which it had lost in the fire were again added a metallic body would result. The question as to whether there be only one or several principles of combustibility was freely discussed, and Stahl decided in favour of the former of these alternatives, and gave to this combustible principle the name Phlogiston (φλογιστός, burnt, combustible).

An example may serve to illustrate the reasoning of the upholders of the Phlogistic theory. Stahl knew that oil of vitriol is a product of the combustion of sulphur; hence sulphur is a combination of oil of vitriol and phlogiston. But this latter is also contained in charcoal, so that if we can take the phlogiston out of the charcoal and add it to the oil of vitriol, sulphur must result. In order that this change may be brought about, the oil of vitriol must be fixed (*i.e.* rendered non-volatile) by combining it with potash; if then the salt thus obtained is heated with charcoal, a *hepar sulphuris* (a compound also produced by fusing potash with sulphur) is obtained. The argument shows that when charcoal is heated with oil of vitriol the phlogiston of the charcoal combines with the oil of vitriol and sulphur is the result. The phlogiston contained in sulphur is not only identical with that contained in charcoal, but also with that existing in the metals, and in all organic bodies, for these are obtained by heating their calces with charcoal, or with oil or other combustible organic substances.

The amount of phlogiston contained in bodies was, according to Stahl, very small, and the greatest quantity was contained in the soot deposited from burning oil. It was likewise considered that the phlogiston given off by combustion is taken up again from the air by plants; and the phenomena of fermentation and decay were believed to depend upon a loss of phlogiston which, however, in this case only escapes slowly. Stahl explains why combustion can only occur in the presence of a good supply of air, because in this case the phlogiston assumes a very rapid whirling motion, and this cannot take place in a closed space.

However false from our present position we see the phlogistic theory in certain directions to be; and although we may now believe that the extension and corroboration of the positive views enunciated by Hooke and Mayow might have led to a recognition of a true theory of chemistry more speedily than the adoption of the theory of phlogiston, we must admit that its rapid general adoption showed that it supplied a real want. It was this theory which for the first time established a common point of view from which all chemical changes could be observed, enabling chemists to introduce something like a system by classing together phenomena which are analogous and are probably produced by the same cause, for the first time making it possible for them to obtain a general view of the whole range of chemical science as then known.

It may appear singular that the meaning of the fact of the increase of weight which the metals undergo on heating, which had been proved by Boyle and others, should have been wholly ignored by Stahl, but we must remember that he considered their *form* rather than their *weight* to be the important and characteristic property of bodies.

Stahl also, perhaps independently, arrived at the same conclusion which Boyle had reached, concerning the truth of the existence of a variety of elementary bodies, as opposed to the Aristotelian or Paracelsian doctrine; and the influence which a clear statement of this great fact by Stahl and his pupils —amongst whom must be mentioned Pott (1692—1777) and Marggraf (1709—1782)—exerted on the progress of the science was immense. It is only after Stahl's labours that a scientific chemistry becomes, for the first time, possible, the essential difference between the teaching of the science then and now being that the phenomena of combustion were then believed to be due to a chemical decomposition, phlogiston being supposed to escape, while we account for the same phenomena now by a chemical combination, oxygen or some element being taken up.

Thus Stahl prepared the way for the birth of modern chemistry. It was on August 1st, 1774, that Joseph Priestley discovered oxygen gas.

Between the date of the establishment of the phlogistic theory by Stahl, and of its complete overthrow by Lavoisier, many distinguished men helped to build up the new science—Black, Priestley, and Cavendish in our own country, Scheele in Sweden, and Macquer in France. The classical researches of Black on the fixed alkalis (1754)[1] not only did much to shake the foundation of the phlogistic theory, but they may be described with truth as the first beginnings of a quantitative chemistry, for it was by means of the balance, the essential instrument of all chemical research, that Black established his conclusions. Up to this time the mild (or carbonated) alkali was believed to be a more simple compound than the caustic alkali. When mild alkali (potashes) was brought into contact with burnt (caustic) lime, the mild alkali took up the principle of combustibility, obtained by the limestone in the fire, and it became caustic. Black showed that in the cases of magnesia-alba and chalk the disappearance of the effervescence on treatment with an acid after heating, was accompanied by a loss of weight. Moreover, as Van Helmont's older observations were quite forgotten, he was the first clearly to establish the existence of a kind of air or gas, termed *fixed air* (1752), totally distinct both from common atmospheric air and from modifications of it, by impurity or otherwise, such as the various gases hitherto prepared were believed to be. This fixed air, then, is given off when mild alkalis become caustic, and is taken up when the reverse change occurs.

This clear statement of a fact, which of itself is a powerful argument against the truth of the theory in which he had been brought up, was sufficient to make the name of Black illustrious, but he became immortal by his discoveries of latent and specific heats, the principles of which he taught in his classes at Glasgow and Edinburgh from 1763. The singularly unbiassed character of Black's mind is shown in the fact that he was the only chemist of his age who completely and openly avowed his conversion to the new Lavoisierian doctrine of combustion. From an interesting correspondence between Black and Lavoisier, it is clear that the great French chemist looked on Black as his master and teacher, speaking of Black's having first thrown light upon the doctrines which he afterwards more fully carried out.[2]

This period of the history of our science has been called that

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[1] "Experiments upon Magnesia-alba, Quicklime, and other Alkaline Substances."—*Edin. Phys. and Literary Essays*, 1755.

[2] *Brit. Assoc. Reports*, 1871, p. 189.

of pneumatic chemistry, because, following in the wake of Black's discovery of fixed air, chemists were now chiefly engaged in the examination of the properties and modes of preparation of the different kinds of airs or gases, the striking and very different natures of which naturally attracted interest and stimulated research.

No one obtained more important results or threw more light upon the existence of a number of chemically different gases than Joseph Priestley. In 1772 Priestley was engaged in the examination of the chemical effect produced by the burning of combustible bodies (candles) and the respiration of animals upon ordinary air. He proved that both these deteriorated the air and diminished its volume, and to the residual air he gave the name of phlogisticated air. Priestley next investigated the action of living plants on the air and found to his astonishment that they possess the power of rendering the air deteriorated by animals again capable of supporting the combustion of a candle.

Fig. 1, a reduced facsimile of the frontispiece to Priestley's celebrated *Observations on Different Kinds of Air*, shows the primitive kind of apparatus with which this father of pneumatic chemistry obtained his results. The mode adopted for generating and collecting gases is seen; hydrogen is being prepared in the phial by the action of oil of vitriol on iron filings, and the gas is being collected in the large cylinder standing over water in the pneumatic trough; round this trough are arranged various other pieces of apparatus, as, for instance, the bent iron rod holding a small crucible to contain the substances which Priestley desired to expose to the action of the gas. In the front is seen a large cylinder in which he preserved the mice, which he used for ascertaining how far an air was impure or unfit for respiration, and standing in a smaller trough is a cylinder containing living plants, the action of which on air had to be ascertained.

On August 1st, 1774, Priestley obtained oxygen gas by heating red precipitate by means of the sun's rays concentrated with a burning glass, and termed it *dephlogisticated* air because he found it to be so pure, or so free from phlogiston, that in comparison with it common air appeared to be impure. Priestley also first prepared nitric oxide (nitrous air or gas), nitrous oxide (dephlogisticated nitrous air), and carbonic oxide; he likewise collected many gases for the first time over mercury, such as ammoniacal gas (alkaline air), hydrochloric acid gas

FIG. 1.

(marine acid air), sulphurous acid gas (vitriolic acid air), and silicon tetrafluoride (fluor acid air).[1] He also observed that when a series of electric sparks is allowed to pass through ammoniacal gas, an increase of volume occurs, and a combustible gas is formed, whilst on heating ammonia with calx of lead phlogisticated air (nitrogen gas) is evolved.

Priestley's was a mind of rare quickness and perceptive powers, which led him to the rapid discovery of numerous new chemical substances, but it was not of a philosophic or deliberative cast. Hence, although he had first prepared oxygen, and had observed (1781) the formation of water, when inflammable air (hydrogen) and atmospheric air are mixed and burnt together in a copper vessel, he was unable to grasp the true explanation of the phenomenon, and he remained to the end of his days a firm believer in the truth of the phlogistic theory, which he had done more than any one else to destroy.

Priestley's notion of original research, which seems quite foreign to our present ideas, may be excused, perhaps justified, by the state of the science in his day. He believed that all discoveries are made by chance, and he compares the investigation of nature to a hound, wildly running after, and here and there chancing on, game (or as James Watt called it, "his random haphazarding"), whilst we should rather be disposed to compare the man of science to the sportsman, who having, after persistent effort, laid out a distinct plan of operations, makes reasonably sure of his quarry.

In some respects the scientific labours of Henry Cavendish (1731-1810) present a strong contrast to those of Priestley; the work of the latter was quick and brilliant, that of the former was slow and thorough. Priestley passed too rapidly from subject to subject even to notice the great truths which lay under the surface; Cavendish made but few discoveries, but his researches were exhaustive, and for the most part quantitative. His investigation on the inflammable air[2] evolved from dilute acid and zinc, tin, or iron, is a most remarkable one. In this memoir we find that he first determined the specific gravity of gases, and used materials for drying gases, taking note of alterations of volume due to changes of pressure and temperature. He likewise proved that by the use of a given weight of each one of these metals, the same volume of inflammable gas

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[1] Priestley's *Observations on Different Kinds of Air*, **1**, 328.

[2] *On Factitious Air.* Hon. Henry Cavendish. *Phil. Trans.* 1766, 141.

can always be obtained no matter which of the acids be employed, whilst equal weights of the metals gave unequal volumes of the gas. Cavendish also found that when the above metals are dissolved in nitric acid, an incombustible air is evolved, whilst if they are heated with strong sulphuric acid sulphurous air is formed. He concluded that when these metals are dissolved in hydrochloric or in dilute sulphuric acid their phlogiston flies off, whilst when heated with nitric or strong sulphuric acids, the phlogiston goes off in combination with an acid. This is the first occasion in which we find the view expressed that inflammable air is phlogiston—a view which was generally held, although Cavendish himself subsequently changed his opinion, regarding inflammable air as a compound of phlogiston and water.

The discovery of oxygen by Priestley, and of nitrogen by Rutherford, naturally directed the attention of chemists to the study of the atmosphere, and to the various methods for ascertaining its composition.

Although Priestley's method of estimating the dephlogisticated air by means of nitric oxide was usually employed, the results obtained in this respect by different observers were very different. Hence it was believed that the composition of the air varies at different places, and in different seasons, and this opinion was so generally adopted, that the instrument used for such measurements was termed a eudiometer (*εὐδία*, fine weather, and *μέτρον*, a measure). Cavendish investigated this subject with his accustomed skill in the year 1781, and found that when every possible precaution is taken in the analysis, "the quantity of pure air in common air is $\frac{10}{48}$," or 100 volumes of air always contain 20·8 volumes of dephlogisticated, and 79·2 volumes of phlogisticated air, and that, therefore, atmospheric air had an unvarying composition. But the discovery which more than any other is for ever connected with the name of Cavendish is that of the composition of water (1781).[1] In making this discovery Cavendish was led by some previous observations of Priestley and his friend Waltire. They employed a detonating closed glass or copper globe holding about three pints, so arranged that an electric spark could be passed through a mixture of inflammable air (hydrogen) and common air,[2] but

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[1] *Phil. Trans.* 1784, 119; 1785, 372. Mr. Cavendish's experiments on air.

[2] A similar apparatus (originally due to Volta) was used by Cavendish. The pear-shaped glass bottle with stopcock, usually called Cavendish's eudiometer, would not be recognised by the great experimenter.

though they had observed the production of water, they not only overlooked its meaning, but believed that the change was accompanied by a loss of weight. Cavendish saw the full importance of the phenomenon and set to work with care and deliberation to answer the question as to the cause of the formation of the water. Not only did he determine the volumes of air and hydrogen, and of dephlogisticated air (oxygen) and inflammable air (hydrogen) which must be mixed to form the maximum quantity of water, but he first showed that no loss of weight occurred in this experiment and that the formation of acid was not an invariable accompaniment of the explosion.

On this important subject it is interesting to hear Cavendish's own words; in the *Philosophical Transactions* fcr 1784, page 128, we read :—

"From the fourth experiment it appears that 423 measures of inflammable air are nearly sufficient to phlogisticate 1,000 of common air; and that the bulk of the air remaining after the explosion is then very little more than four-fifths of the common air employed; so that, as common air cannot be reduced to a much less bulk than that by any method of phlogistication, we may safely conclude when they are mixed in this proportion, and exploded, *almost all the inflammable air and about one-fifth part of the common air, lose their elasticity and are condensed into a dew which lines the glass.*" Since 1,000 volumes of air contain 210 volumes of oxygen and these require 420 volumes of hydrogen to combine with them, we see how exact Cavendish's experiments were. "The better," he continues, "to examine the nature of the dew, 500,000 grain measures of inflammable air were burnt with about 2½ times that quantity of common air and the burnt air made to pass through a glass cylinder eight feet long and three-quarters of an inch in diameter, in order to deposit the dew . . . . By this means upwards of 135 grains of water were condensed in the cylinder, which had no taste or smell, and which left no sensible sediment when evaporated to dryness; neither did it yield any pungent smell during the evaporation; in short it seemed pure water." Cavendish then sums up his conclusions from these two sets of experiments as follows:—"By the experiments with the globe it appeared that when inflammable and common air are exploded in a proper proportion, almost all the inflammable air, and near one-fifth of the common air, lose their elasticity and are condensed into dew. And by this experiment, it appears that this dew is plain water, and consequently that almost all the inflammable air and about one-fifth of the common air are turned into pure water."

Still more conclusive was the experiment in which Cavendish introduced a mixture of dephlogisticated air and inflammable air nearly in the proportions of one to two into a vacuous glass globe, furnished with a stopcock and means of firing by electricity. "The stopcock was then shut and the included air fired by electricity, by which means almost all of it lost its elasticity. By repeating the operation the whole of the mixture was let into the globe and exploded, without any fresh exhaustion of the globe."

Priestley had previously been much led astray by the fact that he found nitric acid in the water obtained by the union of the gases. Cavendish, by a careful series of experiments, explained the occurrence of this acid, for he showed that it did not form unless an excess of dephlogisticated air was used, and he traced its production to the presence in the globe of a small quantity of phlogisticated air (nitrogen) derived from admixture of common air. He likewise proved that the artificial addition of phlogisticated air increased the quantity of acid formed in presence of dephlogisticated air (oxygen), whilst if the latter air were replaced by atmospheric air no acid was formed, in spite of the large amount of phlogisticated air (nitrogen) present. In this way he showed that the only product of the explosion of pure dephlogisticated with pure inflammable air is pure water. Although Cavendish thus distinctly proved the fact of the composition of water, it does not appear from his writings that he held clear views as to the fact that water is a *chemical compound* of its two elementary constituents. On the contrary, he seems to have rather inclined to the opinion that the water formed was already contained in the inflammable air, notwithstanding the fact that in 1783 the celebrated James Watt had already expressed the opinion that "water is composed of dephlogisticated and inflammable air."[1] Cavendish's general conclusions in this matter may be briefly summed up in his own words as follows:—"From what has been said there seems the utmost reason to think that dephlogisticated air is only water deprived of its phlogiston, and that inflammable air, as was before said, is either phlogisticated water, or else pure phlogiston; but in

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[1] Letter from Watt to Black, 21st April, 1783.

all probability the former." To the end of his days Cavendish remained a firm supporter of the phlogistic view of chemical phenomena, but after the overthrow of this theory by Lavoisier's experiments the English philosopher withdrew from any active participation in chemical research.

Whilst Priestley and Cavendish were pursuing their great discoveries in England, a poor apothecary in Sweden was actively engaged in investigations which were to make the name of Scheele (1742-1786) honoured throughout Europe. These investigations, whilst they did not bring to light so many new chemical substances as those of Priestley, and did not possess the quantitative exactitude which is characteristic of the labours of Cavendish, opened out ground which had been entirely neglected, and was perhaps unapproachable by the English chemists. Scheele's discoveries covered the whole range of chemical science. A strong supporter of the phlogistic theory, he held peculiar views (see his celebrated treatise *Ueber die Luft und das Feuer*) as to the material nature of heat and light, and their power of combining with phlogiston, and, like Stahl, he considered modification in the forms of matter to be of much greater importance than alteration in its weight. In experimenting upon the nature of common air he discovered oxygen gas independently of, and probably at least a year before, Priestley, although his discovery was not made public until 1777.

The investigations which led Scheele to this discovery are of interest as a remarkable example of exact observations leading to erroneous conclusions. His object was to explain the part played by the air in the phenomenon of combustion; and for this purpose he examined the action exerted by bodies supposed to contain phlogiston upon a confined volume of air. Thus he found that when a solution of *hepar sulphuris* (an alkaline sulphide) was brought into contact with a given volume of air, that volume gradually diminished, the residual air being incapable of supporting the combustion of a taper. The same result was observed when moist iron filings or the precipitate formed by the action of potash on a solution of green vitriol was employed. Scheele argued that if the effect of the combination of phlogiston with air is simply to cause a contraction, the remaining air must be heavier than common air. He found, however, that it was in fact lighter, and hence inferred that a portion of the common air must have disappeared, and that common air must consist of two gases, one of which has the power of uniting with phlogiston. In order to find out what had become of the portion of air which disappeared, Scheele heated phosphorus, metals, and other bodies in closed volumes of air, and found that these acted just as the former kind of substances had done. Hence he concluded that the compound formed by the union of the phlogiston with one of the constituents of the air is nothing more or less than heat or fire which escapes through the glass. In confirmation of the truth of this hypothesis, Scheele believed that he had experimentally realised the decomposition of heat into phlogiston and fire-air. Nitric acid had, in his belief, a great power of combining with phlogiston, forming with it red fumes; he found that when he heated nitre in a retort, over a charcoal fire, with oil of vitriol, he obtained, in addition to a fuming acid, a colourless air, which supported combustion much better than common air. This he explained by assuming that when charcoal burns, the phlogiston combines with the fire-air to form heat, which passes into the retort, and is there decomposed into phlogiston, which by combining with the acid gave rise to the red nitrous fumes, and pure fire-air. He conceived that he had brought about the same chemical decomposition of heat by warming black oxide of manganese with sulphuric acid, or, still more simply, by heating calx of mercury; for here it was clear enough that by bringing heat and calx of mercury together, the phlogiston combined with the latter, and fire-air was liberated, thus:—

$$\overbrace{\text{Phlogiston} + \text{Fire-air}}^{\text{Heat}} + \text{Calx of Mercury} = \overbrace{\text{Calx of Mercury} + \text{Phlogiston}}^{\text{Mercury}} + \text{Fire-air.}$$

In the year 1774 Scheele made his great discovery of chlorine gas, which he termed dephlogisticated muriatic acid; in the same year he showed that baryta was a peculiar earth; shortly afterwards he proved the separate existence of molybdic and tungstic acids, whilst his investigations of prussian blue led to the isolation of hydrocyanic acid, of which he ascertained the properties. It was, however, especially in the domain of animal and vegetable chemistry that Scheele's most numerous discoveries lay, as will be seen by the following list of organic acids first prepared or distinctly identified by him:—tartaric, oxalic (by the action of nitric acid on sugar), citric, malic, gallic, uric, lactic, and mucic. In addition to the identification of each of these as distinct substances, Scheele discovered glycerin, and we may regard him not only as having given the first indication of the rich harvest to be reaped by the investigation of the compounds of organic chemistry, but as having been the first to discover and make use of characteristic reactions by which closely allied substances can be detected and separated, so that he must be considered one of the chief founders of analytical chemistry.

We have now brought the history of our science to the point at which Lavoisier placed it in the path which it has ever since followed. Before describing the overthrow of the phlogistic theory, it may be well shortly to review the position of the science before the great chemist began his labours little more than one hundred years ago. Chemistry had long ceased to be the slave of the alchemist or the doctor; all scientific chemists had adopted Boyle's definition, and the science was valued for its own sake as a part of the great study of nature. Stahl had well defined chemistry to be the science which was concerned with the resolution of compound bodies into their simpler constituents, and with the building up of compounds from their elements; so that the distinction between pure and applied chemistry was perfectly understood. Geber's definition of a metal as a fusible, malleable substance, capable of mixing with other metals, was still accepted; gold and silver were considered to be pure or noble metals, whilst the other malleable metals, copper, tin, iron, and lead, were called the base metals. Mercury, on the other hand, was thought to be only a metal-like body until it was frozen in 1759. After that date it was considered to be a true metal in a molten state at the ordinary temperature. Arsenic, antimony, bismuth, and zinc, from being brittle, were classed as semi-metals, and to these well-known bodies were added cobalt in 1735, nickel in 1751, and manganese in 1774, whilst platinum was recognised as a peculiar metal in 1750, and molybdenum and tungsten were discovered about 1780. The several metals were supposed to be compounds of phlogiston with metallic calces, whilst sulphur, phosphorus, and carbon were looked upon as compounds of phlogiston with the acids of these elements. Of the simple gases the following were known: inflammable air (hydrogen), supposed to be either pure phlogiston or phlogisticated water; dephlogisticated or fire-air (oxygen); phlogisticated air (nitrogen); and dephlogisticated muriatic acid (chlorine). When the metals dissolve in acids the phlogiston was thought to escape (as inflammable air) either in the pure state or combined with water. It was also known that when a metal is calxed, an increase of weight occurs, but this was explained either by the metal becoming more dense, which, in the opinion of some, would produce an increase of weight, or by the absorption of fiery particles, or again by the escape of phlogiston, a substance which instead of being attracted is repelled by the earth. In short, confusion and difference of opinion in the quantitative relations of chemistry reigned supreme, and it was not until Lavoisier brought his great powers to bear on the subject that light was evoked from the darkness and the true and simple nature of the phenomena was rendered evident.

In the year 1743 Lavoisier was born. Carefully educated, endowed with ample means, Lavoisier, despising the usual occupations of the French youth of his time, devoted himself to science, his genius, aided by a careful mathematical and physical training, rendering it possible for him to bring about a complete revolution in the science of chemistry. Before his time quantitative methods and processes were considered to be purely physical, though they now are acknowledged to be chemical, and of all these, the determination of the weights of bodies taking part in chemical change, as ascertained by the balance, is the most important. Others, indeed, before him, had made quantitative investigations. Black and Cavendish almost exceeded Lavoisier in the exactitude of their experiments, but it is to the French philosopher that the glory of having first distinctly asserted the great principle of the indestructibility of matter belongs. Every chemical change, according to him, consists in a transference or an exchange of a portion of the material constituents of two or more bodies; the sum of the weights of the substances undergoing chemical change always remains constant, and the balance is the instrument by which this fundamental fact is made known.

In his first important research (1770) Lavoisier employs the balance to investigate the question, much discussed at the time, as to whether water on being heated becomes converted into earth. For one hundred and one days[1] he heated water in a closed and weighed vessel; at the end of the experiment the weight of the closed vessel remained unaltered, but on pouring out the water he found that the vessel had lost 17·4 grains, whilst on evaporating the water, he ascertained that it had dissolved 20·4 grains of solid matter. Taking the excess of 3·0

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[1] Œuvres de Lavoisier, 2, 22.

grains as due to unavoidable experimental errors, he concludes that water when heated is not converted into earth. Shortly after this, the same question was examined independently by Scheele, who obtained the same results by help of qualitative analysis, which showed that the water had taken up a constituent of the glass, viz., the alkaline silicates.

When he became acquainted with the novel and unexpected discoveries of Black, Priestley, and Cavendish, a new light burst upon the mind of Lavoisier, and he threw himself instantly with fresh ardour into the study of specially chemical phenomena. He saw at once that the old theory was incapable of explaining the facts of combustion, and by help of his own experiments, as well as by making use of the experiments of others, he succeeded in finding the correct explanation, destroying for ever the theory of phlogiston, and rendering his name illustrious as having placed the science of chemistry on its true basis. On looking back in the history of our science we find indeed that others had made experiments which could only be explained by this new theory, and in certain isolated instances the true explanation may have previously occurred to the minds of others. Thus in 1774 Bayen showed that calx of mercury loses weight, evolving a gas equal in weight to what is lost, and he concludes that either the theory of phlogiston is incorrect, or this calx can be reduced without addition of phlogiston. This, however, in no way detracts from Lavoisier's glory as having been the first to carry out the true ideas consistently and deliberately through the whole science. It is the systematic application of a truth to every part of a science which constitutes a theory, and this it was that Lavoisier and no one else accomplished for chemistry.

When a man has done so much for science as Lavoisier, it seems almost pitiful to discuss his shortcomings and failings. But it is impossible in any sketch of the history of chemistry to ignore the question how far Lavoisier's great conclusions, the authorship of which no one questions, were drawn from his own discoveries, or how far he was indebted to the original investigations of his contemporaries for the facts upon which his conclusions are based. Certain chemists consider that to him alone the foundation of modern chemistry is to be ascribed, both as regards material and deduction, whilst others, affirming that Lavoisier made use of the discoveries of his predecessors, and especially of the discovery of oxygen by Priestley, without acknowledgment, assert that he went so far as to claim for himself a participation in this discovery to which he had no right whatever, and insist that until he had thus obtained, from another, the key to the problem, his views upon the question of combustion were almost as vague as those of the phlogistonists themselves. To enter into a full discussion of the subject would lead us into a historical criticism which would outrun our space. Suffice it to say that many of the charges which have been brought against Lavoisier's good faith unfortunately turn out upon investigation to be well founded, so that whilst we must greatly admire the clear sight of the philosopher, we cannot feel the same degree of respect for the moral character of the man.

His investigations on the phenomena of combustion began in the year 1772. In a first memoir[1] Lavoisier finds not only that when sulphur and phosphorus are burnt no loss of weight occurs, but that an increase of weight is observed. Hence he concludes that a large quantity of air becomes fixed. This discovery leads him to the conclusion that a similar absorption of air takes place whenever a body increases in weight by combustion or calcination. In order to confirm this view, he reduces litharge with charcoal, and finds that a considerable quantity of air is liberated. This, he asserts, appears to him to be one of the most interesting experiments made since the time of Stahl.

Lavoisier's next publication was his *Opuscules physiques et chymiques*, commenced in 1774. In these memoirs he first examines the kind of air given off in the processes of breathing, combustion, and fermentation. The views which he expresses are similar to those put forward long before by Black, to whom he frequently refers as the originator of them, this acknowledgment of his indebtedness to the Scottish philosopher being repeated in the letters from Lavoisier to Black which have been already referred to,[2] in one of which the following passage occurs:—"*Plus confiant dans vos idées que dans les miennes propres, accoutumé à vous regarder comme mon maître,*" &c.

In the year 1774 he describes experiments on the calcination of lead and tin, which he, like Boyle, heats in closed glass globes: so long as the vessel is closed it does not change in weight, but when the neck of the flask is broken, air rushes in,

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[1] *Sur la Cause de l'Augmentation des Poids.* Œuvres **2**, 99.

[2] *British Association Reports*, 1871, 190.

and the weight increases. He further shows that only a portion of the air is taken up by the molten metal, and that the residual air is different from common air, and also from fixed air. From these statements it is clear that Lavoisier considered that the air consists of two different elastic fluids, but that he was not acquainted with Priestley's discovery of oxygen. Nor were his views at this time so precise or well defined as we should gather from reading his papers published in the memoirs of the French Academy for 1774. The explanation is simple enough, inasmuch as owing to the careless and tardy manner in which the memoirs of the French Academy were at that time edited, changes in the original communications were frequently made by the writers before publication, so that the papers printed in the memoirs were corrected to suit alteration in view or in fact which had become known to the authors between the times of reading and of publication.

Thus, for instance, it is clear that the paper[1] detailing the result of his experiments on the calcination of the metals above referred to, which was read before the Academy in Nov. 1774, does not express the same views which we find given in the extended description of his experiments contained in the volume of the memoirs for 1774, which however was not published till 1778. So that although Lavoisier in 1774 considered air to be made up of several different elastic fluids, it is certain that he was not then acquainted with the kind of air which was absorbed in calcination, that his views on the subject were in reality very similar to those expressed a century before by Jean Rey (1630), Mayow (1669), and later, by Pott (1750), and that they were far from being as precise and true as we should gather them to have been from the perusal of his extended memoir, printed in 1778 and corrected so as to harmonise with the position of the science at that date.

It is not until we come to a paper, *Sur le nature du principe qui se combine avec les métaux pendant leur calcination*, first read in 1775 and re-read on Aug. 8, 1778, that we find a distinct mention of oxygen gas, which he first termed "*l'air éminemmment respirable*," or "*l'air pur*," or "*l'air vital*," and that we see that the whole theory of combustion is clear to Lavoisier. He shows that this gas is necessary for the calcination of metals, he prepares it from *precipitatum per se*, as Priestley had previously done, and in the year 1778 we

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[1] *Journal de Physique* for Dec. 1774.

find the first mention of *oxygen* or the acidifiant principle. The name was given to it because he observed that combined with carbon this substance forms carbonic acid, with sulphur vitriolic acid, with nitrous air nitric acid, with phosphorus phosphoric acid, although with the metals in general it produces the metallic calces. In his *Eléments de Chimie*, published in 1782, we find the following words under oxygen gas:—"*Cet air que nous avons découvert presque en même temps, Dr. Priestley, M. Scheele et moi.*"[1] Now there is no doubt whatever that in October, 1774, Dr. Priestley informed Lavoisier, in Paris, of the discovery he had lately made, and that Lavoisier was at that time unacquainted with the fact that *precipitatum per se* yields this new gas on heating. Hence we cannot admit Lavoisier's claim to the joint discovery of oxygen, a claim, it is to be remembered, not made until eight years after the event had occurred. In corroboration of this conclusion we find in Priestley's last work, published in 1800, and singularly enough entitled *The Doctrine of Phlogiston Established*, the following succinct account of the matter. "Now that I am on the subject of the right of discoveries," he says, "I will as the Spaniards say, leave no ink of this kind behind in my ink-horn, hoping it will be the last time I shall have any occasion to trouble the public about it. M. Lavoisier says (*Elements of Chemistry*, English edition, p. 36) 'This species of air (meaning dephlogisticated) was discovered almost at the same time by Mr. Priestley, M. Scheele, and myself.' The case was this: having made the discovery some time before I was in Paris in 1774, I mentioned it at the table of M. Lavoisier, when most of the philosophical people in the city were present; saying that it was a kind of air in which a candle burned much better than in common air, but I had not then given it any name. At this all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise; I told them that I had gotten it from *precipitatum per se* and also from *red lead*. Speaking French very imperfectly, and being little acquainted with the terms of chemistry, I said *plomb rouge* and was not understood till M. Macquer said, 'I must mean *minium*.' M. Scheele's discovery was certainly independent of mine, though I believe not made quite so early."

The two memoirs in which Lavoisier clearly puts forward his views on the nature of combustion and respiration are, first, one read before the Academy in 1775, *Sur la combustion en général*

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[1] Œuvres, 1, 38.

and second, one entitled *Réflexions sur la Phlogistique*, published by the Academy in 1783. In the first of these memoirs he does not attempt to substitute for Stahl's doctrine a rigorously demonstrated theory, but only an hypothesis which appears to him more conformable to the laws of nature, and less to contradict known facts. In the second memoir he develops his theory, denying the existence of any "principle of combustibility," as upheld by Stahl, stating that the metals, and such substances as carbon, sulphur, &c., are simple bodies which on combustion enter into combination with oxygen, and concluding that Stahl's supposition of the existence of phlogiston in the metals, &c., is entirely gratuitous, and more likely to retard than to advance the progress of science.

The triumph of the antiphlogistic (Lavoisierian) doctrines was, however, not complete until the discovery of the compound nature of water by Cavendish in 1781 became fully known. The experiment concerning the combination of hydrogen (phlogiston) and oxygen to form water was at once repeated and confirmed by Lavoisier and Laplace on the 24th June, 1783, and then Lavoisier was able satisfactorily to explain the changes which take place when metals dissolve in acids, and to show that the metals are simple bodies which take up oxygen on combustion, or on solution in acid, the oxygen being derived in the latter case either from the acid or from the water present.

Here, again, if we investigate the position occupied by Lavoisier respecting the discovery of the composition of water we shall see that, not content with the glory of having been the first to give the true explanation of the phenomena, he appears to claim for himself the first quantitative determination of the fact,[1] although it is clear that he had been previously informed by Blagden of Cavendish's experiments.[2]

The verdict concerning the much-vexed question as to the rival claims of Cavendish, Watt, and Lavoisier cannot be more forcibly or more concisely given than in the following words of Professor Kopp—Cavendish first ascertained the facts upon

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[1] Œuvres, **2**, 338.

[2] For an exhaustive discussion of this subject we must refer the reader to George Wilson's *Life of Cavendish*, 1849, as well as to Prof. H. Kopp's *Beiträge zur Geschichte der Chemie. Die Entdeckung der Zusammensetzung des Wassers*, Vieweg und Sohn, 1875. See also Grimaux, *Lavoisier*, F. Alcan, Paris; Thorpe, *Brit. Assoc. Reports*, 1890, *p.* 761, *Historical Essays*, *p.* 110, Macmillan, 1894; and Berthelot, *La Révolution Chimique*, F. Alcan, Paris, 1890.

which the discovery of the composition of water was based, although we are unable to prove that he first deduced from these facts the compound nature of water, or that he was the first rightly to recognise its constituent parts. Watt was the first to argue from these facts the compound nature of water, although he did not arrive at a satisfactory conclusion respecting the nature of the components; whilst Lavoisier, also from these facts, first clearly recognised and stated the true nature of the components of water.

Although at this period the experimental basis of the true theory of combustion was complete, it was some time before the clear statements of Lavoisier were accepted by chemists. Many of those who were most distinguished by their discoveries remained to the last wedded to the old ideas, but by degrees, as fresh and unprejudiced minds came to study the subject, the new views were universally adopted.

In considering this great question from our present point of view, we cannot but recognise in the phlogistic theory the expression of an important fact, of which, however, the true interpretation was unknown to the exponents of the theory. The phlogistonists assert that something which they term phlogiston escapes when a body burns; the antiphlogistonists prove, on the other hand, that no escape of material substance then occurs, but that, on the contrary, an addition of oxygen (or some other element) always takes place. In thus correcting from one aspect the false statement of the followers of Stahl, Lavoisier and his disciples to some extent overlooked an interpretation which may truly be placed upon the statements of the phlogistonists, for if in place of the word "phlogiston" we read "energy," this old theory becomes the expression of the latest development of scientific investigation. We now know that when two elements combine, *Energy*, generally in the form of heat, is usually evolved, whilst in order to resolve the compound into its constituent elements an expenditure or absorption of an equal amount of energy is requisite.

The fact that every distinct chemical compound possesses a fixed and unalterable composition, was first proved by the endeavour to fix the composition of certain neutral salts. Bergman from the year 1775, and Kirwan from 1780, were occupied with this experimental inquiry, but their results did not agree sufficiently well to enable chemists to come to a satisfactory conclusion, and it is to Cavendish that we owe the first proof that the combining proportion between base and acid follows a distinct law, whilst to him we also owe the introduction of the word "equivalent" into the science. It is, however, to Richter (1762–1807) that we are indebted for the full explanation of the fact, that when two neutral salts undergo mutual decomposition, the two newly-formed salts are also neutral. He shows in his "Stöchiometrie," that the proportions by weight of different bases which saturate the same weight of a given acid will also saturate a different but a constant weight of a second acid. So that if we have determined what weight of a given base is required to saturate a given weight of several different acids, and if we also know the weights of the different bases which are needed for the neutralisation of a given weight of any one of these acids, we can calculate in what proportion each of these bases will unite with any one of these acids. Richter also showed that when the different metals are separately dissolved in the same quantity of sulphuric acid, each one takes up the same quantity of oxygen; or, as we may now express it, the varying quantities of these different oxides which neutralise one and the same quantity of any acid, all contain the same quantity of oxygen. These important observations attracted but little attention or consideration from Richter's contemporaries, all of whom were busily engaged in carrying on the phlogistic war in which he himself took an active part in defence of the older doctrine.

The investigations of Richter and his predecessors had reference mainly to the proportions by weight in which acids and bases unite, which, according to Lavoisier's theory, are not simple substances, whilst Lavoisier recognised the fact that the elements themselves combine in definite proportions by weight. In opposition to this view of combination in definite unalterable quantities, L. Claude Berthollet published in 1803 his celebrated *Essai de statique Chimique*, in which he refers the phenomena of chemistry to certain fundamental properties of matter, endeavouring to explain chemical changes by the motions of the particles of matter on the same principles as Newton's theory of gravitation accounts for the simpler motions of the heavenly bodies. Considering chemical change from this mechanical point of view, Berthollet pointed out the circumstances under which we can accomplish the highest development of the science, namely, prediction of phenomena; and if, in his assumed identity of the laws of gravitation and chemical action, he was mistaken, the aim which he set before himself is that which has remained, and will ever remain, the highest ideal of the science. The influence which Berthollet's views exercised on the progress of the science was less powerful than it otherwise would have been owing to the fact that he, considering chemical combination to be based upon purely mechanical laws, was obliged to admit that an alteration of the conditions, such as mass and temperature, must generally produce an alteration in the proportion in which two elements combine. He was, therefore, forced to the conclusion that combination may take place, as a rule, between variable proportions of the elements, with the formation of a series of compounds differing gradually in composition, combination in a limited number of proportions being the exception, due to some special physical property of the compound containing those proportions, such as insolubility or elasticity. The opposite view that combination only takes place in a small number of definite fixed proportions was defended by his countryman Proust, and this led to a keen debate between the two French philosophers which lasted from the year 1801 to the year 1808. In the end, however, Proust proved conclusively that Berthollet's views were not generally applicable, inasmuch as he showed that when one metal gives rise to two oxides, the weight of the metal which combines with the same quantity of oxygen to form the various oxides is a different but a fixed quantity, so that combination does not take place by the gradual addition of one element, but by sudden increments. It must, however, be remembered that Berthollet's views are strictly applicable to that class of homogeneous mixtures now known as physical mixtures[1] (p. 50).

Proust's observations might in fact have led him to the recognition of the law of multiple proportions, but his analyses were not sufficiently accurate for this purpose,[2] so that neither Proust nor Richter arrived at the true expression of the facts of chemical combination, and it was reserved for John Dalton, (1766—1844) clearly to state the great law of chemical combination in multiple proportions, and to establish a theory which is in full accord with the observed facts.

Democritus, and after him Epicurus and Lucretius, had long ago taught that matter is made up of small indivisible particles, and the idea of the atomic constitution of matter, and even the

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[1] On this subject see Hartog, *Nature* (1894) **50**, 149.

[2] *Journal de Physique*, **59**, 260 and 321.

belief that chemical combination consists in the approximation of the unlike particles, had been already expressed by Kirwan in 1783, as well as by Higgins in 1789. Dalton was, however, the first to propound a truly *chemical* atomic theory, the only one hitherto proposed which co-ordinates the facts of chemical combination in a satisfactory manner. The cardinal point upon which Dalton's atomic theory rests, and in which it differs from all previous suggestions, is that it is a *quantitative* theory respecting the constitution of matter, whereas all others are simply qualitative views. For whilst all previous upholders of an atomic theory, including even Higgins, had supposed that the relative weights of the atoms of the various elements are the same, Dalton at once declared that the atoms of the different elements are not of the same weight; and that the *relative atomic weights of the elements are the proportions by weight in which the elements combine, or some multiple or submultiple of these.*

Dalton published his first table of atomic weights of certain elements and their compounds, as an appendix to a paper read before the Manchester Literary and Philosophical Society, Oct. 21, 1803, and issued in 1805, on the absorption of gases by water and other liquids.

Dalton's First Table of the Relative Weights of the Ultimate Particles of Gaseous and other Bodies.[1]

Hydrogen	1
Azot	4·2
Carbon	4·3
Ammonia	5·2
Oxygen	5·5
Water	6·5
Phosphorus	7·2
Phosphuretted hydrogen	8·2
Nitrous gas	9·3
Ether	9·6
Gaseous oxide of carbon	9·8
Nitrous oxide	13·7
Sulphur	14·4
Nitric acid	15·2
Sulphuretted hydrogen	15·4
Carbonic acid	15·3
Alcohol	15·1
Sulphureous acid	19·9
Sulphuric acid	25·4
Carburetted hydrogen, from stagnant water	6·3
Olefiant gas	5·3

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[1] Certain inaccuracies in the values of the weights of some of the compounds occur in this table; thus, 4·2 + 5·5 = 9·7, whilst 9·3 appears opposite nitrous gas. Whether these are merely printer's errors or are to be explained in some other way can now only be conjectured. See Roscoe on Dalton's First Table of Atomic Weights. *Manchester Lit. and Phil. Soc. Mem.* 1874–5. *3rd Series*, 5, 269.

As a reason for introducing these numbers, Dalton states that the different solubility of gases in water depends upon the weight and number of the ultimate particles of the several gases. "The inquiry," he continues, "into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new; I have lately been prosecuting this inquiry with remarkable success. The principle cannot be entered upon in this paper, but I shall subjoin the results as far as they appear ascertained by my experiments."

Thus then, at the end of a paper on a physical subject, does Dalton make known a principle the discovery of which at once placed the science of chemistry upon a firm basis, and has rendered the name of its discoverer second only to that of Lavoisier amongst the founders of the science.

It is not easy to follow in detail the mental or experimental processes by which Dalton arrived at this great theory. Certain it is, however, that the idea which lay at its foundation had long been in his mind, which was essentially of a mathematical and mechanical turn, and that it was by his own experimental determinations, and not by combining any train of reasoning derived from the previous conclusions of other philosophers that he was able to prove the correctness of his theory. Singularly self-reliant, accustomed from childhood to depend on his own exertions, Dalton was a man to whom original work was a necessity.[1] In the preface to the second part of his *New System of Chemical Philosophy*, published in 1810, he clearly shows his independence and even disregard of the labours of others, for he says—"Having been in my progress so often misled by taking for granted the results of others, I have determined to write as little as possible but what I can attest by my own experience."

It appears from entries in his laboratory notebooks[2] that Dalton, being actively engaged upon the question of atomic weights in September, 1803, had drawn up at least three provisional tables before that printed in the Manchester Memoirs. He appears to have been mainly influenced in the development of his theory by the consideration of the physical properties of gases, and more especially by his attempts to account for the various phenomena of the diffusion and the

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[1] Lonsdale's *Life of Dalton*. Longmans, 1874.

[2] *A New View of the Origin of Dalton's Atomic Theory*, p. 26. Roscoe and Harden. (Macmillan, 1896.)

solubility of gases, rather than by the results of any extended series of chemical analyses.

His views on these subjects, in fact, led him to endeavour to ascertain the relative sizes of the particles in different gases, and this involved the determination of the *relative weight* of the particles of each gas and the relative number contained in a given volume. It was with the object of determining this relative weight that he had recourse to the chemical composition of the gas, and was thus led to the ideas which he formulated as the Atomic Theory.

As early as 1802, in an experimental inquiry into the proportions in which the several gases constituting the atmosphere occur, Dalton clearly points out "that the element of oxygen may combine with a certain portion of nitrous gas" (our nitric oxide) "or with twice that portion, but with no intermediate quantity," and this observation, no doubt, also contributed largely to the development of his views.[1]

The atomic theory and the law of combination in multiple proportions were publicly announced by Dalton at a lecture delivered at the Royal Institution[2] in London in 1803–4, but, singularly enough, first became widely known through the agency of his friend, Professor Thomas Thomson, of Glasgow, who published in 1807 an account of Dalton's discovery in the third edition of his *System of Chemistry*.[3] In the following year (1808) Dalton made known his own views in the remarkable book entitled *A New System of Chemical Philosophy*, in which (Part i, p. 213) he says—"It is one great object of this work to show the importance and advantage of ascertaining the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle."

Dalton at once applied his views to the composition of water, ammonia, nitrous gas (nitric oxide), nitrous oxide, nitric acid, sulphurous and sulphuric acids, and the oxides of carbon, and,

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[1] *Manchester Memoirs*, 2nd Series, 1, 250.

[2] New System. Part I. Preface.

[3] Thomson's statement that the law of multiple proportions was discovered by the study of olefiant gas and marsh gas is now known to be inaccurate. (Debus, *On Some of the Fundamental Laws of Chemistry*, Cassel, 1894; Roscoe and Harden, *loc. cit.*).

somewhat later, to nitrous acid, olefiant gas and marsh gas, phosphuretted hydrogen, alcohol and ether, and he showed and expressed by the numbers given in his tables that the composition of these might be most simply explained by the assumption that one atom of one element is attached to 1, 2, 3, &c., atoms of another. The novelty and importance of his view of the composition of chemical compounds induced Dalton to introduce a method of graphic representation of the atoms of the elements, and the system he adopted may be illustrated by a reproduction of the plate (p. 39) and description appended to the first part of his New System.

Plate IV.—This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites	46
2	Azote	5	12	Barytes	68
3	Carbone or charcoal	5	13	Iron	38
4	Oxygen	7	14	Zinc	56
5	Phosphorus	9	15	Copper	56
6	Sulphur	13	16	Lead	95
7	Magnesia	20	17	Silver	100
8	Lime	23	18	Platina	100
9	Soda	28	19	Gold	140
10	Potash	42	20	Mercury	167

21	An atom of water or steam, composed of 1 of oxygen and 1 hydrogen, retained in physical contact by a strong affinity and supposed to be surrounded by a common atmosphere of heat; its relative weight	8
22	An atom of ammonia, composed of 1 of azote and 1 of hydrogen	6
23	An atom of nitrous gas, composed of 1 of azote and 1 of oxygen	12
24	An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen	6
25	An atom of carbonic oxide, composed of 1 of carbone and 1 of oxygen	12
26	An atom of nitrous oxide, 2 azote + 1 oxygen	17
27	An atom of nitric acid, 1 azote + 2 oxygen	19
28	An atom of carbonic acid, 1 carbone + 2 oxygen	19

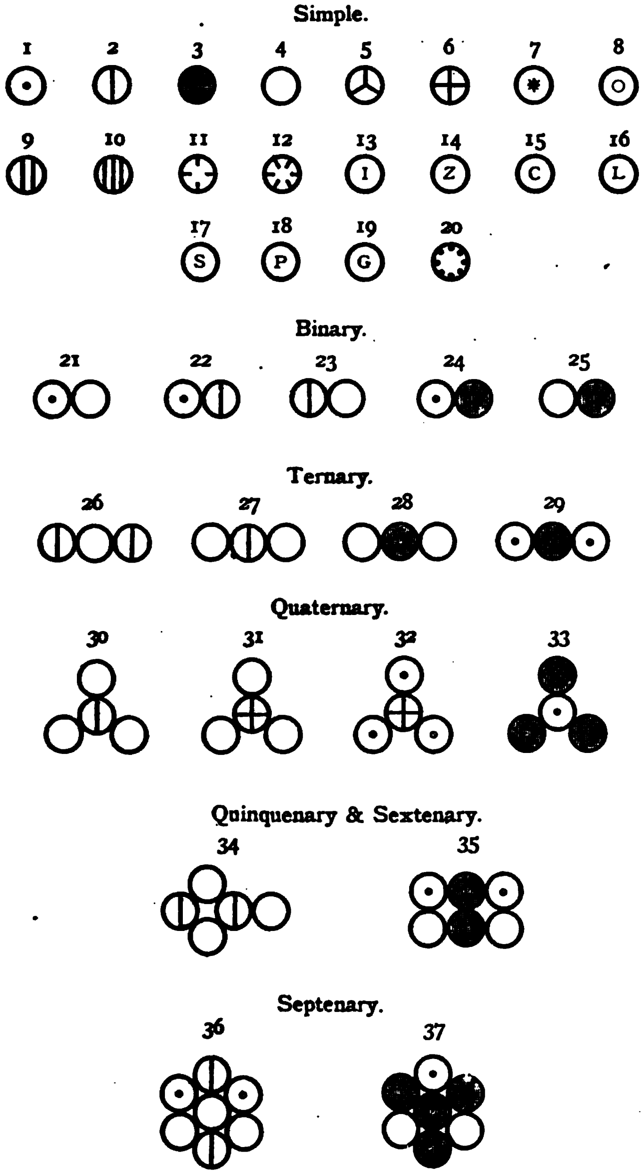
Simple.
1 2 3 4 5 6 7 8
9 10 11 12 13 14 15 16
17 18 19 20
I Z C L S P G
Binary.
21 22 23 24 25
Ternary.
26 27 28 29
Quaternary.
30 31 32 33
Quinquenary & Sextenary.
34 35
Septenary.
36 37

Fig.		
29	An atom of carburetted hydrogen, 1 carbone + 2 hydrogen	7
30	An atom of oxynitric acid, 1 azote + 3 oxygen	26
31	An atom of sulphuric acid, 1 sulphur + 3 oxygen	34
32	An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen	16
33	An atom of alcohol, 3 carbone + 1 hydrogen	16
34	An atom of nitrous acid, 1 nitric acid + 1 nitrous gas	31
35	An atom of acetous acid, 2 carbone + 2 water	26
36	An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water	33
37	An atom of sugar, 1 alcohol + 1 carbonic acid	35

These atomic weights, it is evident, are far from being those which we now accept as correct, indeed they are different from those given in his first table, for Dalton not only frequently altered and amended these numbers, according as his experiments showed them to be faulty, but even distinctly asserts the doubtful accuracy of some. Chemists at that time did not possess the means of making accurate determinations, and when we become acquainted with the rough methods which Dalton adopted, and the imperfect apparatus he had to employ, we cannot but be struck with the clearness of his vision and the boldness of grasp which enabled him, thus poorly equipped, to establish a doctrine which further investigation has only more firmly established, and which, from that time forward, has served as the pole star round which all other chemical theories revolve.

Amongst those to whose labours we are indebted for advancing Dalton's atomic theory are Thomas Thomson and Wollaston, but before all, the great Swedish chemist Berzelius, to whom we owe the first really exact values for these primary chemical constants. With remarkable perseverance he ascertained the exact composition of a large number of compounds, and was, therefore, able to calculate the combining weights of many elements, thus laying the foundation-stones of the science as it at present exists. In 1818 Berzelius published his theory of chemical proportions, and of the chemical action of electricity, and in these remarkable works he made use of chemical symbols and formulæ such as we now employ, to denote not only the qualitative, but also the quantitative composition of chemical compounds. From this time forward it was satisfactorily proved and generally acknowledged that the elementary bodies combine together either in certain given proportions by weight, or in simple multiples of these proportions; and, through the researches of Berzelius and others, the list of elements, which at the time of Lavoisier amounted to twenty-three in number, was considerably increased.

Next in order comes Humphry Davy's discovery of the compound nature of the alkalis (1808), proving that they are not simple substances but oxides of peculiar metals, and thus entirely revolutionising the views of chemists as to the constitution of a large and important class of compounds, including the salts of the alkaline earths. The discussion in 1810 as to the constitution of chlorine—then termed oxygenated muriatic acid—decided by Davy and Gay-Lussac in favour of its elementary nature, was likewise a step of the greatest importance and of wide application. In 1811 iodine was discovered by Courtois, and most carefully investigated by Gay-Lussac, who proved the close analogy existing between this element and chlorine. The discovery of many other elements now opened out fresh fields for investigation, and gave the means of classifying those already known. The names and properties of these will be found in the portions of this book specially devoted to their description.

If Dalton, as we have seen, succeeded in placing the laws of chemical combination by *weight* on a firm basis, to Gay-Lussac belongs the great honour of having discovered the law of the combination of gaseous bodies by *volume*. In the year 1805 Gay-Lussac and Alexander von Humboldt found that one volume of oxygen combines with exactly two volumes of hydrogen to form water, and that these exact proportions hold good at whatever temperature the gases are brought into contact. This observation was extended by Gay-Lussac, who in 1808 published his celebrated memoir on the combination of gaseous bodies,[1] in which he proves that gases not only combine in very simple relations by volume, but also that the alteration of volume which these gases undergo in the act of combination may be expressed by a very simple law. Hence it follows that the densities of gases must bear a simple relation to their combining weights. The true explanation of these facts was first given by Avogadro in 1811, and his hypothesis is now universally admitted both by chemists and physicists. According to the Italian philosopher the number of smallest particles or molecules contained in the

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[1] *Mémoires d'Arcueil*, 1808, **2**, 207.

same volume of every kind of gas is the same, similar circumstances of pressure and temperature being of course presupposed.

The discovery by Gay-Lussac of the laws of volume-combination, together with Avogadro's explanation of the law, served no doubt as most valuable supports of Dalton's atomic theory, but the truth of this latter theory was still further asserted by a discovery made by Dulong and Petit in 1819. These French chemists determined the specific heat of thirteen elementary bodies and found that the numbers thus obtained, when compared with the atomic weights of the same bodies, showed that the *specific heats* of the several elements are inversely proportional to their atomic weights, or in other words, the atom of each of these elements possesses the same capacity for heat. Although subsequent research has shown that this law does not apply in every case, it still remains a valuable means of controlling the atomic-weight determinations of many elements.

In the same year a discovery of equal importance was announced by Mitscherlich—that of the law of *Isomorphism*. According to this law, chemically analogous elements can replace each other in many crystalline compounds, either wholly or in part, in atomic proportions without any change occurring in the crystalline form of the compound. This law, like that of atomic heats, has proved of great value in the determination of atomic weights.

Gradually the new basis given by Dalton to our science was widely extended by these discoveries and by the researches of other chemists, and a noble structure arose, towards the completion of which a numerous band of men devoted the whole energies of their lives.

Especially striking was the progress made during these years in the domain of Organic Chemistry, or the chemistry of the substances found in, or obtained from, vegetable or animal bodies. Analytical results were wanting to prove that the complicated Organic bodies followed the same laws as the more simple Inorganic compounds. It is to Berzelius that we owe the proof that this is really the case, and his exact analyses placed organic chemistry in this respect on a firm and satisfactory basis. There still remained, however, much doubt as to the strict identity of the laws according to which organic and inorganic compounds were severally formed. Most of the compounds met with in mineral chemistry could be easily prepared by the juxtaposition of their constituents; they were of comparatively simple constitution, and could as a rule be prepared by synthesis from their constituent elements. Not so with organic bodies; they appeared to be produced under circumstances wholly different from those giving rise to mineral compounds; the mysterious phenomena of life seemed in some way to influence the production of these substances and to preclude the possibility of their artificial preparation. A great step was therefore made in our science when, in 1828, Wöhler artificially prepared urea, a body which up to that time had been thought to be a product peculiar to animal life. This discovery broke down at once the supposed impassable barrier between organic and mineral chemistry, pointed out the rich harvest of discovery since so largely developed, especially by Liebig, in the synthesis of organic substances, and paved the way to the knowledge which we have gained, chiefly through the labours of the last-named chemist, that the science of Physiology consists simply in the Chemistry and Physics of the body.

GENERAL PRINCIPLES OF THE SCIENCE

1 **Matter** is capable of assuming three different states or conditions:—the solid, the liquid, and the gaseous. Of these, the first two have, for obvious reasons, been recognised from the earliest ages, as accompanying very different kinds of substances. It is, however, only within a comparatively short time that men have come to understand that just as there are many distinct kinds of solids and liquids, so there are many distinct kinds of gases (Van Helmont). These may, indeed, be colourless and invisible, but, nevertheless, they can readily be shown to differ one from another. Thus, Black, in 1752, collected a peculiar gas, which we now know as carbonic acid gas, or carbon dioxide, obtained by the action of dilute acids on marble; to this gas he gave the name of "fixed air," because it is fixed in the alkaline carbonates, which at that time were called the mild alkalis, in contradistinction to the caustic alkalis. This invisible gas does not, like air, support the combustion of a taper, and, unlike air, it renders clear lime-water turbid; it is also much heavier than air, as can be shown by pouring it downwards from one vessel to another, by drawing it out of a vessel by means of a syphon, or by pouring it into a beaker glass previously equipoised at one end of the beam of a balance (see Fig. 2). That the gas has actually been poured out is seen either by a burning taper being extinguished when dipped into the beaker glass, or by adding some clear lime-water, which then turns milky.

In 1766, Cavendish showed that the gas termed by him inflammable air, and obtained by the action of dilute acids on metallic zinc or iron, is also a peculiar and distinct substance, to which we now give the name of hydrogen gas. It is so much lighter than air that it may be poured upwards, and takes fire when a light is brought in contact with it, burning with a pale blue flame. Soap-bubbles blown with hydrogen ascend in the air, and if hydrogen be poured upwards into the equipoised bell-jar hung mouth downwards on the arm of the balance (Fig. 3). the equilibrium will be disturbed, and the arm with the bell-jar will rise.

On August 1st, 1774, Priestley heated some red precipitate (oxide of mercury) and obtained from it a new colourless gas called oxygen, and this, although invisible, possesses properties quite different from those of air, carbonic acid gas, or hydrogen gas. A red hot chip of wood is at once rekindled when plunged into this gas, and bodies such as iron wire or steel watch-spring, which do not burn in the air, burn with brilliancy in oxygen.

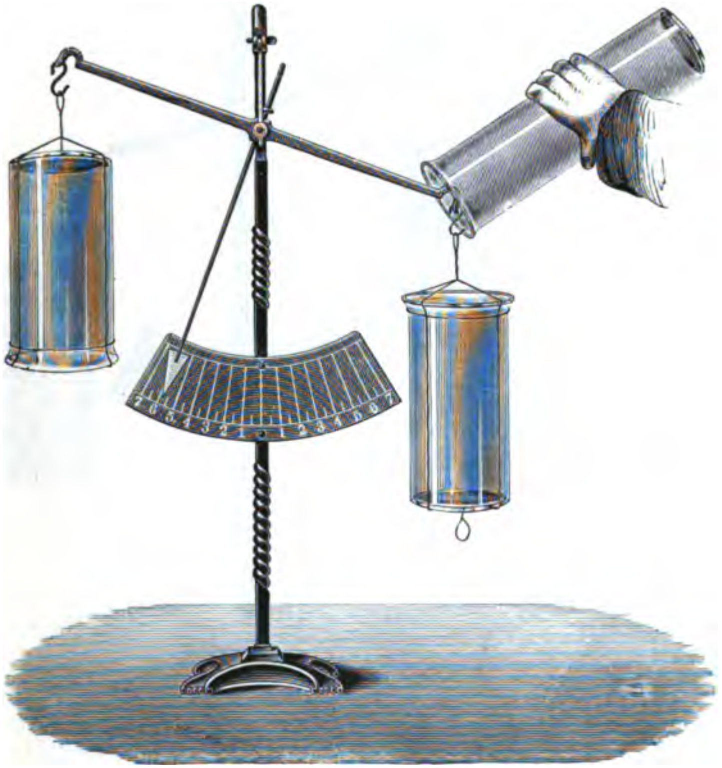

Fig. 2.

These examples suffice to show that invisible gases exist which differ in the widest degree from each other, though many more illustrations of the same principle might be given.

2 The method which we have had to adopt in order thus to discern differences between these invisible gases, is termed the *Experimental Method.* Experiments may be said to be questions put to nature, and a science is termed experimental, as opposed to observational, when we are able so to control and modify the conditions under which a phenomenon occurs as to be able to observe the effect of each modification, and thus to gain a clearer insight into the true sequence of events which constitutes the phenomenon under examination.

FIG. 3.

Chemistry is, therefore, one of several experimental sciences, each of which has the study of natural phenomena for its aim. These sciences are most intimately connected, or, rather, the division into separate sciences is quite arbitrary, so that it is not possible exactly to say where the phenomena belonging to one science begin and those appertaining to another science end.

Nature is a connected whole, and the divisions which we are accustomed to make of natural phenomena into separate sciences serve only to aid the human mind in its efforts to arrange a subject which is too vast in its complete extent for the individual to grasp. Although it may not be possible exactly to define the nature of the phenomena which we class as *chemical*, as distinguished from those termed *physical*, it is not difficult, by means of examples, to obtain a clear idea of the kind of observations with which the chemist has to do. Thus, for instance, it is found that when two or more given substances are brought together, under certain conditions they may change their properties, and a new substance, differing altogether from the original ones, may make its appearance, Or, again, a given substance may, when placed under certain conditions, yield two or more substances differing entirely from the original one in their essential properties. In both these cases the change which occurs is termed a chemical change; if several distinct substances have coalesced to form one new substance, an act of *chemical combination* is said to have occurred; if one substance is made to yield two or more distinct new bodies, a *chemical decomposition* has taken place. These acts of chemical union and disruption occur alike amongst solid, liquid, and gaseous bodies; they depend in the first place on the essential nature of the substances, and secondly, on the circumstances or conditions under which they are placed. It is also to be observed, in the first place, that these actions of chemical union do not occur when the component particles are situated at a distance from each other, close approximation being necessary in order that such changes should take place; whilst secondly we invariably notice that both combinations and decompositions are attended with some change in the energy of the system, such as an evolution or absorption of heat, or the production of light, or of a current of electricity; finally it is characteristic of chemical union that complete combination does not occur between any proportions of the substances which may be taken, but only between certain definite proportions (see p. 63).

3 Some simple illustrations of chemical action may here be cited. When powdered sulphur and fine copper-filings are well mixed together, a green-coloured powder results, in which, however, a microscope will show the particles of sulphur lying by the side of the particles of copper. On heating this green

powder in a test tube, the mass suddenly becomes red-hot, and, on cooling, a uniform black powder is found. This is neither copper nor sulphur, but a chemical compound of the two, in which no particle of either of the substances can be seen, however high a magnifying power be employed, but from which, by the employment of certain chemical means, both copper and sulphur can again be extracted. Here, then, we have a case of chemical combination between two solid bodies, well characterised by change of properties and evolution of heat and light.

Again, if the two gases, hydrogen and oxygen, be mixed together in equal volumes and an electric spark produced in them, they combine with an explosion to form water, which condenses as a liquid; a large amount of heat is evolved, a flash of light is seen, and a considerable contraction in volume occurs. Complete combination, however, only occurs when hydrogen is mixed with exactly half its volume of oxygen; if either of the gases be in excess of this proportion the excess remains uncombined, so that in the present case half of the oxygen would remain free and unaltered.

The water formed by the combination of the two gases can again be decomposed into free hydrogen and oxygen, and this can readily be effected by a current of electricity, as discovered by Nicholson and Carlisle in 1800. For the purpose of exhibiting this we only need to pass a current of electricity from four or six Grove's or Bunsen's elements by means of two platinum poles through some water acidulated with sulphuric acid (Fig. 4). The instant contact is made, bubbles of gas begin to ascend from each platinum plate and collect in the graduated tubes, which at first are filled with the acidulated water. After a little time it will be seen that the plate which is in connection with the zinc of the battery evolves more gas than the one which is in contact with the platinum or carbon of the battery; and after the evolution has continued for a few minutes one tube will be seen to contain twice as much gas as the other. On examination, the larger volume of gas will be found to be hydrogen, and will take fire and burn when a light is brought to the end of the tube in which it was collected, whilst the smaller volume of gas is seen to be oxygen, a glowing chip of wood being rekindled when plunged into it.

Whereas the combination of hydrogen with oxygen is attended by the evolution of energy in the forms of light and heat, the inverse change, the decomposition of water, requires energy to be supplied, and in the experiment just described, this is conveyed to the water in the form of the energy of the electrical current.

As regards these transformations of energy which accompany chemical change, it must be remembered that according to the well-established law of the "Conservation of Energy"[1] the total amount of energy in the universe is constant and never varies. Energy cannot be created, but energy of one kind can be transformed into energy of a different kind, and it is a change of this sort which accompanies chemical action.

FIG. 4.

Free hydrogen and oxygen, therefore, possess a store of potential energy, known by the name of *chemical energy* (or potential energy of chemical separation), and when combination occurs this is converted into the energy of heat and light. On the other hand, when water is decomposed, as described above,

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[1] See Clerk Maxwell, *Theory of Heat*. Chap. IV.

the energy of the electrical current is converted into the chemical energy of the mixture of hydrogen and oxygen which is produced.

4 It is not always an easy matter to decide whether a particular change can properly be termed chemical, although in cases like the foregoing there is no difficulty in arriving at a decision. The phenomena of solution, for example, exhibit many of the characteristics of chemical change. Thus, water dissolves a solid substance like sugar, forming a homogeneous, colourless liquid, which differs both from sugar and from water itself in properties; heat is absorbed during the process of solution, and water at any particular temperature will not dissolve more than a definite proportion of sugar, any excess of the latter being left undissolved and unchanged. On the other hand, it is possible, by the gradual addition of sugar to water, to obtain a series of solutions, the properties of which pass *gradually* from those of pure water to those of a saturated solution of sugar, and in this respect, therefore, the phenomenon differs from a true chemical change. Solutions accordingly are usually looked upon, not as true chemical compounds, but as *physical mixtures*, other examples of the same class being found in many of the alloys formed by fusing together two or more metals. In the examination of homogeneous substances as they occur in nature or are artificially produced it is usually the chemist's first task, and it is often one of extreme difficulty, to ascertain whether the material in question is a chemical individual or a physical mixture of two or more distinct substances.

5 In many cases of chemical action, the products are gaseous, whilst at least one of the materials acted upon is solid or liquid. Hence, in these cases, a disappearance or apparent loss of matter occurs. It has, however, been shown by many accurate experiments that in these cases the loss of matter is only apparent, so that chemists have come to the conclusion that *matter is indestructible*, and that in all cases of chemical action in which matter disappears, the loss is apparent only, the solid or liquid being changed into an invisible gas, the weight of which is, however, exactly identical with that of its component parts. We only require to allow a candle to burn for a few minutes in a clean flask filled with air in order to show that the materials of the candle, hydrogen and carbon, unite with the oxygen of the air to form, in the first place, water, which is seen in small drops bedewing the bright sides of the flask, and in the second,

carbon dioxide or carbonic acid gas, whose presence is revealed to us by lime-water being thereby turned milky. The fact that the sum of the weights of the products of combustion (water and carbon dioxide) is greater than the loss of weight sustained by the candle is clearly shown by an experiment made by means of the apparatus (Fig. 5), which consists of a tube equipoised on the arm of a balance. In the long vertical tube a taper is placed, the other end of the system being attached to a gasholder filled with water, which, on being allowed to run out, causes a current of air to pass through the tube, and thus maintains the combustion of the taper. The water and carbonic acid gas which are formed are absorbed in the bent tube, which contains caustic potash. After the taper has burnt for a few minutes, the apparatus is disconnected from the gasholder and allowed to vibrate freely, when it will be found to be appreciably heavier than it was before the taper had burnt, the

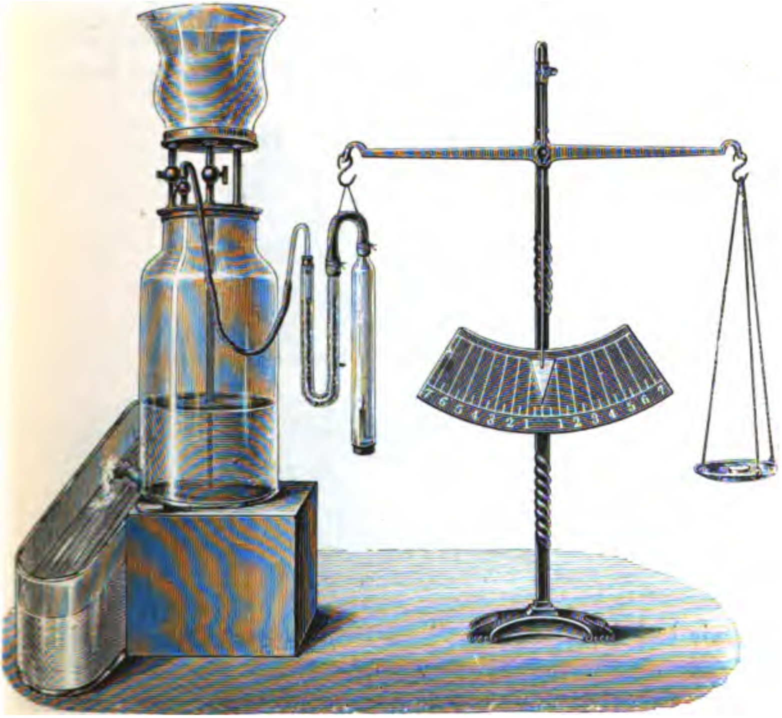

FIG. 5.

explanation being that the excess of weight is due to the combination of the carbon and hydrogen of the wax with the oxygen of the air.

6 Another series of experiments which shows more plainly the fact of the indestructibility of matter, and is of historical interest, is that by which it has been clearly demonstrated that the air consists of two different gases, oxygen and nitrogen. The fact of the complex nature of air was proved by Priestley in 1772 by setting fire, by means of a burning glass, to charcoal contained in a vessel of air. He showed that fixed air (carbonic acid gas) was produced, and that on the absorption of this fixed air by lime-water, one-fifth of the original bulk of the air had disappeared, and a colourless gas remained, which did not support combustion or respiration. It was not, however, till the year 1775, after he had discovered oxygen, that Priestley distinctly stated that this gas was contained in common air, and about the same time Scheele came to an identical conclusion from independent experiments. But the method by which the existence of oxygen in the air was first demonstrated in the clearest way, is that adopted by Lavoisier, and described in his *Traité de Chimie.*[1] Into a glass balloon (Fig. 6) having a long straight neck, Lavoisier brought 4 ounces of pure mercury; he then bent the neck so that when the balloon rested on the top of the furnace, the end of the bent neck appeared

FIG. 6.

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[1] Part i. chap. iii.

above the surface of the mercury contained in the trough, thus placing the air in the bell-jar in communication with that in the balloon. The volume of the air (reduced to 28 inches of mercury and a temperature of 10°) contained in the bell-jar and balloon amounted to 50 cubic inches. The mercury in the balloon was now heated, by a fire placed in the furnace, to near its boiling point. For the first few hours no change occurred, but then red-coloured specks and scales began to make their appearance. Up to a certain point these increased in number, but after a while no further formation of this red substance could be noticed.

FIG. 7.

After heating for twelve days the fire was removed, and the volume of the air was seen to have undergone a remarkable diminution: the volume, measured under the same conditions as before, having been reduced from 50 to between 42 and 43 cubic inches. The red particles were next carefully collected, and on weighing, were found to amount to 45 grains. These 45 grains were next introduced into a small retort connected with a graduated glass cylinder (Fig. 7), and on heating they yielded 41½ grains of metallic mercury and from 7 to 8 cubic inches of a gas which was found to be pure oxygen. Thus, the whole of the oxygen which was withdrawn from the air by the mercury, was obtained again when the oxide formed was decomposed by heat.

7 The statement that matter is indestructible, it must be remembered, is based entirely upon the evidence of experiment, and many investigations have been carried out to test its validity. These have taken the form of weighing two substances, such as silver and iodine (Stas), mercury and iodine (Kreichgauer), or iodine and sodium sulphite (Landolt), as carefully as possible, and then allowing them to unite or react chemically and finally weighing the products. In the experiments of Stas the silver and iodine were separately dissolved and allowed to react, and the resulting silver iodide was then collected and weighed, but in the other cases the chemical change was allowed to occur within sealed-up vessels, so that no mechanical loss could take place. The result has been that no definite change of weight has in any case been observed.[1] The accuracy of the statement that matter is indestructible is therefore true within the limits of accurate weighing which have at present been attained.

8 It is not merely to the investigation of changes occurring in the essential properties of inorganic or mineral matter that the chemist has to direct his attention. The study of many of the phenomena observed in the vegetable or animal world also claim his notice. So much so, indeed, is this the case that the science of physiology has been defined as the physics and chemistry of the body. The simplest as well as the most complicated changes which accompany life are, to a great extent, chemical in character, and, although we are still unable fully to explain many of these changes, yet each year brings us additional aid, so that we may expect some day to possess an exact knowledge of the chemistry of life. In order to be convinced that vital actions are closely connected with chemical phenomena, we only need to blow the air from our lungs through clear lime-water to see from the ensuing turbidity of the water that carbonic acid gas is evolved in large quantities during the process of the respiration of animals, and when we further observe that the higher animals are all warmer than surrounding objects, we come to the conclusion that the process of respiration is accompanied by oxidation, and that the breathing animal

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[1] Stas, *Nouvelles Recherches sur les Lois des Proportions Chimiques* (1865), 152; Landolt, *Zeit. physikal. Chem.* (1893) **12**, 1-33; Kreichgauer, quoted by Landolt.

resembles the burning candle, not only in the products of this combustion, viz., water and carbon dioxide, but in the heat which that combustion evolves, the difference being that in the one case the oxidation goes on quickly and is confined to one spot (the wick of the candle), whereas in the other it goes on slowly and takes place throughout the body. In like manner the living plant is constantly undergoing changes, which are as necessary for its existence as the act of breathing is for animals. One of the most fundamental of these changes is readily seen if we place some fresh green leaves in a bell-jar filled with spring water and expose the whole to sunlight. Bubbles of gas are observed to rise from the leaves, and these, when collected, prove to be oxygen. In presence of the sunlight the green leaf has decomposed the carbonic acid gas held in solution in the spring water, assimilating the carbon for the growth of its body and liberating the oxygen as a gas. Nor, indeed, are the investigations of the chemist now confined to the organic and inorganic materials of the earth which we inhabit. Recent research has enabled him, in conjunction with his colleague the physicist, to obtain a knowledge of the chemistry as well as of the physics of the sun and far distant stars, and thus to found a truly cosmical science.

9 It is the aim of the chemist to examine the properties of all the different substances which occur in nature, so far as they act upon each other, or can be made to act so as to produce something different from the substances themselves; to ascertain the circumstances under which such chemical changes occur, to discover the laws upon which they are based, and to investigate the relation between the properties of substances and their chemical composition. In thus investigating terrestrial matter it is found that all the various forms of matter with which we are surrounded, or which have been examined, can be divided into two great classes.

I. ELEMENTARY BODIES.—Elements, or simple substances, out of which no other two or more essentially differing substances have been obtained.

II. COMPOUND BODIES, or compounds, out of which two or more essentially differing substances have been obtained.

Only twenty-three elements were known during the lifetime of Lavoisier; now we are acquainted with not less than seventy-eight. Of these, and their compounds with each other, the whole mass of our globe, solid, liquid, and gaseous, is composed, and these elements contribute the material out of which the fabric of our science is built.

The following is an alphabetical list of the elementary bodies known at present (1904), together with their atomic weights (see also p. 76).

LIST OF ELEMENTS.

	ATOMIC WEIGHT.	
	H=1.	O=16.
Aluminium..Al	26·9	27·1
Antimony ..Sb	119·3	120·2
Argon ......A	39·6	39·9
Arsenic ......As	74·4	75·0
Barium ..... Ba	136·4	137·4
Bismuth ...Bi	206·9	208·5
Boron.........B	10·9	11
Bromine ...Br	79·36	79·96
Cadmium ...Cd	111·6	112·4
Cæsium ......Cs	131·9	132·9
Calcium ...Ca	39·8	40·1
Carbon C	11·91	12·00
Cerium ......Ce	139·2	140·25
Chlorine ...Cl	35·18	35·45
Chromium...Cr	51·7	52·1
Cobalt ......Co	58·56	59·0
Columbium (Niobium)..Cb(Nb)	93·3	94
Copper ......Cu	63·1	63·6
Erbium ......Er	164·8	166
Fluorine ...F	18·9	19
Gadolinium .Gd	155	156
Gallium .....Ga	69·5	70
Germanium.Ge	71·9	72·5
Glucinum (Beryllium)Gl(Be)	9·03	9·1
Gold ....Au	195·7	197·2
Helium ......He	4	4
Hydrogen...H	1·000	1·008
Indium ......In	113·1	114
Iodine I	125·90	126·85
Iridium......Ir	191·5	193·0
Iron ....Fe	55·5	55·9
Krypton ...Kr	81·2	81·8
Lanthanum.La	137·9	138·9
Lead ....Pb	205·35	206·9
Lithium......Li	6·98	7·03
Magnesium..Mg	24·18	24·36
Manganese..Mn	54·6	55·0
Mercury......Hg	198·5	200·0
MolybdenumMo	95·3	96·0
Neodymium.Nd	142·5	143·6
Neon ....Ne	19·9	20
Nickel ......Ni	58·3	58·7
Nitrogen ...N	13·93	14·04
Osmium ...Os	189·6	191
Oxygen ......O	15·88	16·00
Palladium...Pd	105·7	106·5
Phosphorus.P	30·77	31·0
Platinum ...Pt	193·3	194·8
Potassium ..K	38·86	39·15
Praseodymium...Pr	139·4	140·5
Radium......Ra	223·3	225
Rhodium ...Rh	102·2	103·0
Rubidium ..Rb	84·8	85·4
Ruthenium.Ru	100·9	101·7
Samarium...Sm	148·9	150
Scandium ...Sc	43·8	44·1
Selenium ...Se	78·6	79·2
Silicon ......Si	28·2	28·4
Silver ....Ag	107·12	107·93
Sodium ......Na	22·88	23·05
Strontium...Sr	86·94	87·6
Sulphur......S	31·83	32·06
Tantalum ...Ta	181·6	183
Tellurium ...Te	126·6	127·6
Terbium ...Tb	158·8	160
Thallium ...Tl	202·6	204·1
Thorium ...Th	230·8	232·5
Thulium ...Tm	169·7	171
Tin............Sn	118·1	119·0
Titanium ...Ti	47·7	48·1
Tungsten ...W	182·6	184·0
Uranium ...U	236·7	238·5
Vanadium ..V	50·8	51·2
Xenon X	127	128
Ytterbium..Yb	171·7	173·0
Yttrium ...Yt	88·3	89·0
Zinc ....Zn	64·9	65·4
Zirconium...Zr	89·9	90·6

In addition to the above, the existence of many other elements has been announced, among which are Holmium, Yttrium-*a*, and the radio-active Polonium. These, however, have not, as yet, been very perfectly investigated, and their atomic weights and chemical relationships remain undetermined.

10 For the sake of convenience it is customary to divide the elements into two classes—the *Metals* and the *Non-Metals*, a distinction which was first made about the time of Lavoisier, when only a few elements were known. Now, however, the division is a purely arbitrary one, as it is not possible to draw an exact line of demarcation between these two groups, so that there are cases in which an element has been considered as a metal by some chemists and as a non-metal by others. To the first class belong such substances as gold, silver, mercury, and tin; to the second substances which are gaseous at the ordinary temperature, such as hydrogen, nitrogen, and oxygen, together with certain solid bodies, as carbon and sulphur. The number of metals is much larger than that of the non-metals: we are acquainted with fifty-eight metals, and with only twenty non-metals.

11 In this treatise the elements usually classed as non-metals are considered in the present volume, arranged in the following groups:

	Symbol.		Symbol.
Hydrogen	H	Nitrogen	N
		Phosphorus	P
Fluorine	F	Arsenic	As
Chlorine	Cl		
Bromine	Br	Boron	B
Iodine	I		
		Carbon	C
Oxygen	O	Silicon	Si
Sulphur	S		
Selenium	Se	Helium	He
Tellurium	Te	Neon	Ne
		Argon	A
		Krypton	Kr
		Xenon	X

The metals are treated in the second volume according to the groups and sub-groups of the Periodic System of Classification, which is there fully discussed. (Vol. II. (1897), p. 37.)

12 Of the elements only five occur largely in the air, about thirty have been detected in the sea, whilst all the seventy-eight are found irregularly distributed throughout the solid mass of our planet.

Some are very abundant, and are widely distributed, whilst others have hitherto been found only in such minute quantities and so seldom, that even their properties have not yet been satisfactorily examined. Thus oxygen is found throughout the air, sea, and solid earth in such quantities as to make up nearly half the total weight of the crust of our planet, whilst the compounds of cæsium, although tolerably widely distributed, occur only in very minute quantity, and those of erbium have as yet been met with only in very small quantities, and in very few localities.

In order to obtain an idea as to which elements form the main portion of the solid crust of the earth, we may examine the composition of all the different kinds of granitic or eruptive rocks which constitute by far the greater part of the earth's crust. From analyses made by Bunsen we find that all granitic rocks possess a composition varying between the limits given in the following table, so that these numbers give a fair idea of what is known of the average chemical composition of the solid crust of the globe. All the other elements occur in quantities less than any of those mentioned in the table.

The Composition of the Earth's Solid Crust in 100 *parts by weight.*

Oxygen . .	44·0 to 48·7	Calcium . . .	6·6 to 0·9
Silicon . .	22·8 „ 36·2	Magnesium . .	2·7 „ 0·1
Aluminium .	9·9 „ 6·1	Sodium . . .	2·4 „ 2·5
Iron . . .	9·9 „ 2·4	Potassium . .	1·7 „ 3·1

13 In considering for the first time the subject of the elements, the question will at once suggest itself—Are these seventy-eight all the elements which make up our earth, or is it likely that other hitherto undiscovered elements exist? Judging from analogy, remembering what has previously occurred, and looking to the incomplete state of our knowledge concerning the composition of the earth's crust, we may fairly conclude that it is all but certain that other elementary bodies remain to be discovered. Every improve-

ment in our methods of examination leads to the detection either of new elements or of old ones in substances in which they had previously been overlooked. Thus by the methods of *Spectrum Analysis* many new elements have been discovered, including cæsium, rubidium, thallium, indium, and gallium, and the existence of several others rendered highly probable especially among the rare earths. By help of this method we are also enabled to come to certain conclusions respecting the distribution and occurrence of these same elements in some of the heavenly bodies, and we learn that many of the metals, and even non-metals, which are well known to us on the earth, are found in the sun and the fixed stars. The conclusion that the terrestrial elements exist beyond the bounds of our planet is borne out by the chemical examination of the meteoric stones which are constantly falling upon the surface of the earth. In hundreds of these which have been examined, no single case of the discovery of an unknown element has occurred. The substances of which meteorites have been found to consist are iron, nickel, oxygen, calcium, silicon, carbon, and other well-known terrestrial elements.

Special interest attaches to the discovery of the element Helium in terrestrial matter, since this name was first given to the unknown element to which certain lines in the spectrum of the solar chromosphere were ascribed by Lockyer in 1868, and it was not until 1895 that it was discovered by Ramsay in the rare mineral Cléveite.

14 Another question which may here be asked is—Are these elements really undecomposable substances? and to this it may be replied, that so far as our chemical knowledge enables us to judge, we may assume, with a considerable degree of probability, that by the application of more powerful means than are at present known, chemists will succeed in obtaining still more simple bodies from the so-called elements. Indeed, if we examine the history of our science, we find frequent examples occurring of bodies which only a short time ago were considered to be elementary which, upon more careful examination, have been shown to be compounds.

The singular fact that the element radium, which belongs to the newly discovered class of radio-active substances, continually emits a radio-active emanation, which itself slowly changes into helium, is a phenomenon of the highest interest in this connection. It is more fully discussed on a later page.

15 A very remarkable fact observed in the case of many elements is that they are capable of existing in more than one distinct condition, presenting totally different physical qualities. One of the most striking examples of these *allotropic modifications* or conditions of matter (ἄλλος, another—τρόπος, a way or mode) occurs with carbon, which exists as *Diamond*, *Graphite*, and *Charcoal*, bodies which as regards colour, hardness, specific gravity, &c., bear certainly but a slight resemblance to each other, but which, when they are burnt in oxygen, all give the same relative weight of the same product, viz., carbonic acid, thereby proving their chemical identity.

16 *The Balance.*—As it is the aim of the chemist to examine the properties of the elements and their compounds, and as the weight-determination of a substance is of the greatest importance, it becomes necessary for him to ascertain with great precision the proportion by weight in which these several elements combine, as well as that in which any one of them occurs in a given compound, and for this purpose the *Balance* is employed. By means of this instrument the weight of a given substance is compared with the unit of weight. It consists essentially of a light but rigid brass beam (Fig. 8), suspended on a fixed horizontal axis situated at its centre; and this beam is so hung as to assume a horizontal position when unloaded. At each end of the beam scale-pans are hung, one to receive the body to be

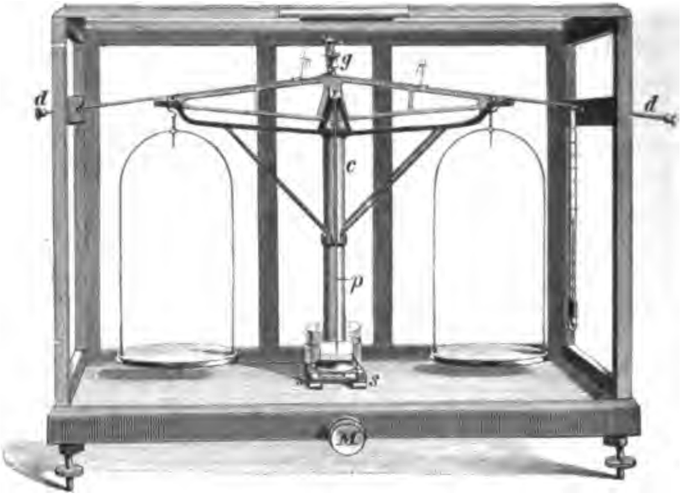

FIG. 8.

weighed and the other for the weights. When each pan is equally weighted the beam must still retain its horizontal position or oscillate about this position, but when one pan is more heavily weighted than the other, the beam will incline on the side of the heavier pan. The balance is, therefore, a lever with equal arms, and it is evident that the weight of the substance relative to the unit weight employed is the sum of the weights necessary to bring the balance into equilibrium. The two important requisites in a balance are (1) accuracy, (2) sensibility, and these can only be gained by careful construction. It needs but little consideration to see that in a delicate balance the friction of the various parts must be reduced to a minimum. This is usually accomplished by suspending the beam by means of an agate knife-edge, working on an agate plane, whilst the pans are attached to each end of the beam by a somewhat similar arrangement shown in Fig. 9. The position of the axis of suspension relatively to the centre of gravity of the beam is likewise a matter of consequence. If the axis of suspension and the centre of gravity in a balance were coincident, the beam would remain stationary in all positions in which it might be placed. If the axis of suspension be placed below the centre of gravity the beam would be in a condition of unstable equilibrium. Hence the only case in which the balance can be used is that in which the point or axis of suspension is above the centre of gravity, for in this case alone will the beam return to a horizontal position after making an oscillation, and in this case the balance may be considered as a pendulum, the whole weight of the beam and pans being regarded as concentrated at the centre of gravity. In order that the weight of the substance and the sum of the measuring weights in the scale-pan

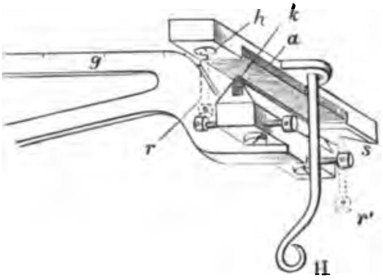

Fig. 9.

may be equal, it is evident that the axis of suspension must be exactly in the centre of the beam, or in other words, that the balance must have arms of equal length. It is also necessary that the balance should have great sensibility; that is, that it may be moved by the smallest possible weight; for this end it is likewise requisite that the vertical distance of the centre of gravity below the axis of suspension should be as small as possible. As the whole weight of the instrument may be regarded as concentrated at the centre of gravity, it evidently requires a less force to act at the end of the beam to move the instrument when the distance of the centre of gravity from the point of suspension of the balance is small, than when that distance is greater, inasmuch as in the latter case the weight has to be lifted through a longer arc. The sensibility of the balance is also increased, both by increasing the length of the beam and by diminishing the weight of the beam and of the load. When, however, the beam is made either too long or too light it ceases to be rigid, and a serious source of error is introduced.

In all weighings with delicate balances it is necessary to have recourse to the method of weighing by vibration[1] by which the excursions of the moving beam are accurately observed instead of its approach to the horizontal position.

A good chemical balance, such as is commonly used for analytical work will indicate 0·0001 gram,[2] when loaded with 50—100 grams in each pan. With a specially constructed balance by combining this method of vibrations with that of double weighing, which consists in reversing the position of the loads in the two pans, it is possible with a load of 1 kilogram in each pan to ascertain definitely a difference of weight of 0·0001 gram or the 1/10,000,000 of the weight in either pan.[3]

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[1] See Prof. W. H. Miller, *Phil. Trans.* 1856, 763; and article "Balance," *Watts' Dictionary*, 1st Edition.

[2] For a table of equivalent values of the common English weights and measures with those of the metrical system, see Appendix to this volume.

[3] Landolt, *Zeit. physikal. Chem.* (1893), **12**, 1.

LAWS OF CHEMICAL COMBINATION.

17 The composition of a chemical compound can be ascertained in two ways: (1) By separating it into its component elements, an operation termed *analysis* (*ἀναλύω*, I unloose), and (2) by bringing the component elements under conditions favourable to combination, an operation termed *synthesis* (*συντίθημι*, I place together). In both of these operations the balance is employed; the weight of the compound and of the components in each instance must be ascertained, except indeed in the case of certain gases of known specific gravity, when a measurement of the volume occupied by the gas may be substituted for a determination of its weight.

It is one of the aims of *analytical chemistry* to ascertain with great precision the percentage composition of all chemical substances, and this branch of inquiry is termed *quantitative analysis*, as contradistinguished from that which has only to investigate the kind of material of which substances are composed, and which is hence termed *qualitative analysis*.

COMBINATION BY WEIGHT.

18 The first great law discovered by the use of the balance, is that *the elements combine with one another in a limited number of definite proportions*, this number being almost invariably found by experiment to be a small one. When two elements are brought together under such conditions that they can combine, it is always found that one or more of a small number of compounds is produced, the particular substance or substances formed depending upon the special circumstances of the experiment. Thus carbon is found to be capable of uniting with oxygen in two different proportions, producing two distinct substances, carbonic acid gas and carbon monoxide, these being the only compounds of carbon with oxygen which are known. Some elements, on the other hand, only form one compound with each other, whilst others again form a large number. Each one of these compounds is found to have a fixed composition, containing the elements of which it is made up in a definite proportion by weight, and this fixity of composition is used as a characteristic of a chemical compound as opposed to a mere mechanical mixture, the constituents of which may be present in any vari-

able proportions. In whatever way the conditions under which the elements are made to combine may be varied, it is always found that they unite in exactly the same ratio, unless, as sometimes happens, the changed conditions are favourable to the production of one of the small number of other compounds which can be formed by the same elements. Thus, for instance, the combination of silver with chlorine has been brought about in no less than four different ways, but in every case it has been found that the resulting compound contains 107·12 parts of silver for 35·18 of chlorine.[1] The combination of chlorine with phosphorus, on the other hand, takes place in two distinct ratios, so that when an excess of phosphorus is present, the resulting compound contains 10·25 parts of this element for 35·18 parts of chlorine, whilst if the latter be kept in excess, this weight of it only combines with 6·15 parts of phosphorus. These are, however, the only two compounds of these elements which are known. In like manner hydrogen combines with oxygen to yield water, a substance which contains 88·81 parts of oxygen to 11·19 of hydrogen. If these elements are brought together in proportions differing from those in which they are present in water, the excess of one element remains in the free state; thus, if 98·81 parts of oxygen by weight be brought ogether with 11·19 parts of hydrogen under circumstances in which they can combine, 88·81 parts of the oxygen will combine with all the hydrogen to form 100 parts of water, whilst 10 parts of oxygen remain in the free state.

It will therefore be seen that the chemical combination of two or more elements does not result in the production of a series of compounds varying gradually in composition, according to the conditions of the experiment, but yields one or more compounds, each of which contains its constituents in a perfectly fixed and definite ratio.[2]

19 As has been said, the case frequently occurs of two elements uniting to form several compounds, for each of which the law of definite proportion holds good, and the special relations which exist between the weights of the two elements entering into combination under these circumstances were first discovered by John Dalton. Thus the two elements, carbon and oxygen, unite to form two distinct compounds, carbonic oxide gas and carbonic acid gas, and 100 parts of each of these bodies are

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[1] Stas, *Récherches*, etc. pp. 108, 210. 1865.

[2] On this subject compare Hartog, *Nature*, 1894, **50**, 149.

found by analysis to contain the following weights of the elements:—

	Carbonic Oxide Gas.	Carbonic Acid Gas.
Carbon	42·86 . . .	27·27
Oxygen	57·14 . . .	72·73
	100·00	100·00

Knowing these facts Dalton asked himself what was the relation of one element (say of the oxygen) in both compounds when the other element remained constant? He thus found that, in proportion to the carbon, the one compound contained exactly double the quantity of oxygen which the other contained; thus:—

	Carbonic Oxide Gas.	Carbonic Acid Gas.
Carbon	10·0 . . .	10·0
Oxygen	13·3 . . .	26·6
	23·3	36·6

Thus again, analysis showed that two compounds which carbon forms with hydrogen, viz., marsh gas and olefiant gas, have the following percentage composition:—

	Marsh Gas.	Olefiant Gas.
Carbon	74·95 . . .	85·68
Hydrogen	25·05 . . .	14·32
	100·00	100·00

Dalton then calculated how much hydrogen is combined in each compound with 10 parts by weight of carbon, and he found that in olefiant gas there are 1·67 parts by weight of hydrogen to 10 of carbon, whilst marsh gas contains 3·34 parts of hydrogen to the same quantity of carbon, or exactly double as much.

As another example we may take the compounds of nitrogen and oxygen, of which no less than five are known to exist. The percentage composition of these five bodies is found by experiment to be as follows:—

	(1)	(2)	(3)	(4)	(5)
Nitrogen . .	63·71	46·75	36·91	30·51	25·99
Oxygen . .	36·29	53·25	63·09	69·49	74·01
	100·00	100·00	100·00	100·00	100·00

If then, like Dalton, we inquire how much oxygen is contained in each of these five compounds, combined with a fixed weight, say 10 parts of nitrogen, we find that this is represented by the numbers 5·7, 11·4, 17·1, 22·8, and 28·5. In other words, the relative quantities of oxygen are in the ratio of the simple numbers 1, 2, 3, 4, and 5.

20 The above examples illustrate the relations exhibited in the combination of two or more of the elements to form compounds, but a careful examination of the quantitative composition of a whole series of chemical compounds leads to a further conclusion respecting the nature of the laws of chemical combination which is of the highest importance. Let us examine the composition of any given series of compounds as determined by analysis, such as the following:—

CHLORIDES.

Hydrogen Chloride.		Potassium Chloride.	
Chlorine	97·24	Chlorine	47·51
Hydrogen	2·76	Potassium . . .	52·49
	100·00		100·00

Sodium Chloride.		Silver Chloride.	
Chlorine	60·59	Chlorine	24·72
Sodium	39·41	Silver	75·28
	100·00		100·00

BROMIDES.

Hydrogen Bromide.		Potassium Bromide.	
Bromine	98·76	Bromine	67·13
Hydrogen . . .	1·24	Potassium . . .	32·87
	100·00		100·00

Sodium Bromide.		Silver Bromide.	
Bromine	77·62	Bromine	42·56
Sodium	22·38	Silver	57·44
	100·00		100·00

Iodides.

Hydrogen Iodide.		Potassium Iodide.	
Iodine	99·21	Iodine	76·41
Hydrogen	0·79	Potassium . . .	23·59
	100·00		100·00

Sodium Iodide.		Silver Iodide.	
Iodine	84·62	Iodine	54·03
Sodium	15·38	Silver	45·97
	100·00		100·00

Arranged in this way we do not notice any simple relation existing between the components of this series, except that the quantity of hydrogen is always smaller than that of the chlorine, bromine, or iodine, whilst the quantity of sodium is always smaller than that of potassium, and this again is less than the quantity of silver.

21 If, however, instead of examining a constant weight of the several compounds we ask ourselves how much of the one constituent in each compound combines with a constant weight of that constituent which is common to several, we shall obtain at once a clear insight into the law of the formation of the compound. In the series of hydrogen compounds, for instance, let us calculate (by simple proportion) how much chlorine, bromine, and iodine combine with the unit weight of hydrogen. We then obtain for the composition of these compounds:—

Hydrogen Chloride.		Hydrogen Bromide.		Hydrogen Iodide.	
Chlorine . .	35·18	Bromine .	79·36	Iodine . .	125·90
Hydrogen .	1·00	Hydrogen .	1·00	Hydrogen .	1·00
	36·18		80·36		126·90

Continuing our calculation, let us next ask how much of the metals, potassium, sodium, and silver, unite with 35·18 parts by weight of chlorine to form chlorides; with 79·36 parts of bromine to form bromides, and with 125·90 parts of iodine to form iodides. The result is as follows:—

Chlorides.

Potassium Chloride.		Sodium Chloride.		Silver Chloride.	
Chlorine .	35·18	Chlorine .	35·18	Chlorine .	35·18
Potassium .	38·86	Sodium .	22·88	Silver . .	107·12
	74·04		58·06		142·30

Bromides.

Potassium Bromide.		Sodium Bromide.		Silver Bromide.	
Bromine .	79·36	Bromine .	79·36	Bromine .	79·36
Potassium .	38·86	Sodium .	22·88	Silver . .	107·12
	118·22		102·24		186·48

Iodides.

Potassium Iodide.		Sodium Iodide.		Silver Iodide.	
Iodine . .	125·90	Iodine . .	125·90	Iodine . .	125·90
Potassium.	38·86	Sodium. .	22·88	Silver . .	107·12
	164·76		148·78		233·02

Now for the first time a remarkable relation becomes apparent, for it is clear that the SAME weights of the metals potassium, sodium, and silver, which combine with 35·18 parts of chlorine to form chlorides, also combine with 79·36 parts of bromine to form the bromides, and with 125·90 parts of iodine to form the iodides. In other words, if we replace the 35·18 parts by weight of chlorine in each of these compounds by 79·36 parts of bromine, we get the bromides, and if by 125·90 parts of iodine we obtain the iodides of the metals. Hence one and the same weight of metals (38·86 of potassium, 22·88 of sodium, and 107·12 of silver) has the power of forming compounds with the precise quantities of chlorine, bromine, and iodine respectively, which unite with 1 part by weight of hydrogen, to form the hydrides of these elements. These quantities of the elements in question are called *equivalent quantities*, because they are the amounts of them which will combine with the same weight of some other element.

38·86	of potassium	combine with	35·18 of chlorine 79·36 „ bromine 125·90 „ iodine	respectively.
22·88	„ sodium	„ „	„	„
107·12	„ silver	„ „	„	„
1·00	„ hydrogen	„ „	„	„

Similar results are obtained from the examination of the compounds of all the other elements, so that a number may be assigned to each element which is termed the *combining weight* or *equivalent weight* of the element.

22 Taking an example from another group of chemical compounds we find that the well-known oxides of hydrogen, lead, copper, mercury, and cadmium possess the following percentage composition:—

OXIDES.

Water.		Lead Oxide.		Copper Oxide.	
Hydrogen .	11·19	Lead . .	92·82	Copper .	79·89
Oxygen . . .	88·81	Oxygen .	7·18	Oxygen .	20·11
	100·00		100·00		100·00

Mercury Oxide.		Cadmium Oxide.	
Mercury	92·63	Cadmium . . .	87·54
Oxygen	7·37	Oxygen	12·46
	100·00		100·00

Whilst the corresponding sulphides exhibit the following composition:

SULPHIDES.

Sulphuretted Hydrogen.		Lead Sulphide.		Copper Sulphide.	
Hydrogen .	6·01	Lead. . .	86·58	Copper . .	66·48
Sulphur . .	93·99	Sulphur .	13·42	Sulphur .	33·52
	100·00		100·00		100·00

Mercury Sulphide.		Cadmium Sulphide.	
Mercury	86·18	Cadmium . . .	77·81
Sulphur	13·82	Sulphur	22·19
	100·00		100·00

23 If, as before, we now compare the quantity of each element united with one and the same weight of oxygen, taking 7·94 parts of this element, because this is the amount of it which combines with one part of hydrogen and is, therefore, the equivalent weight of oxygen with respect to hydrogen, we get the following numbers :—

Water.		Lead Oxide.		Copper Oxide.	
Hydrogen .	1·00	Lead . .	102·68	Copper . .	31·55
Oxygen . .	7·94	Oxygen .	7·94	Oxygen . .	7·94
	8·94		110·62		39·49

Mercury Oxide.		Cadmium Oxide.	
Mercury . . .	99·25	Cadmium	55·80
Oxygen . . .	7·94	Oxygen	7·94
	107·19		63·74

And, if we investigate the sulphides, we find that one and the same weight of sulphur, viz. 15·91 parts by weight, unites with weights of these elements to form sulphides, which are identical with the amounts that combined with 7·94 parts by weight of oxygen to form oxides. Thus we have :—

Sulphuretted Hydrogen.		Lead Sulphide.		Copper Sulphide.	
Hydrogen .	1·00	Lead . .	102·68	Copper . .	31·55
Sulphur . .	15·91	Sulphur .	15·91	Sulphur .	15·91
	16·91		118·59		47·46

Mercury Sulphide.		Cadmium Sulphide.	
Mercury	99·25	Cadmium . . .	55·80
Sulphur	15·91	Sulphur . . .	15·91
	115·16		71·71

Hence we see again that the amounts of these elements which unite with an equivalent of oxygen also combine with an equivalent of sulphur, so that

1 part by weight of hydrogen	combines with	7·94 of oxygen 15·91 of sulphur
102·68 parts by weight of lead	combine with	„
31·55 „ „ „ „ copper	„	„
99·25 „ „ „ „ mercury	„	„
55·80 „ „ „ „ cadmium	„	„

and these are, therefore, the equivalent weights of these elements.

24 When one element combines with another in more than one proportion it is said to have more than one equivalent, and since the amounts of one element which combine with a fixed weight of a second are in a simple ratio to one another, it follows that the several equivalents of an element must also stand in a simple ratio to one another. Iron for example forms several different compounds with oxygen, two of which have the following composition as determined by analysis:—

	Ferrous Oxide.	Ferric Oxide.
Iron	77·54	69·97
Oxygen	22·46	30·03
	100·00	100·00

Calculating the amount of iron combined with the equivalent (7·94 parts) of oxygen we find

	(1)	(2)
Iron	27·75	18·50
Oxygen	7·94	7·94
	35·69	26·44

These amounts of iron are, however, in the simple ratio of 2 : 3, 27·75 being the equivalent of iron in ferrous oxide and 18·50 in ferric oxide.

25 It will be seen, therefore, that *combination always takes place between certain definite and constant proportions of the elements or between multiples of these.*

26 At a time when the question of combination in a limited

number of definite proportions was still under discussion, John Dalton's speculative mind conceived an hypothesis which clearly explained the law of combination in constant proportions, and solved the question as to the nature of the compounds formed by the union of two or more elements in several different proportions. The hypothesis known as *Dalton's Atomic Theory* may be said to have become one of the most important foundation stones of the science, and to have exerted an influence on its progress greater than that of any other generalisation, with perhaps the single exception of Lavoisier's explanation of the phenomena of combustion, and the discovery of the indestructibility of matter.

The Atomic Theory, then, follows the doctrines of the Greek philosophers so far as it supposes that matter is not continuous, but made up of extremely small individual particles termed atoms (*a* privative and τέμνω I cut); but differs from that of the ancients and becomes truly a chemical atomic theory inasmuch as it supposes the atoms of different elements not to possess the same weights, but to be characterised by different weights. Thus the atom of oxygen is 15·88 times as heavy as the atom of hydrogen, and the weights of the atoms of oxygen and chlorine are as 15·88 to 35·18. Dalton assumed, in the second place, that chemical combination consists in the approximation of the individual atoms to each other. Having made these assumptions he was able to understand why combination always takes place between certain amounts of the elements or between multiples of these amounts; since combination being supposed to take place between some number of atoms of each of the elements which unite, it follows that the amounts which combine must be some finite multiple of the weights of the atoms.

It is thus clear that the atomic theory accounts for the formation of all compounds which are found to exist, but it is equally evident that it in no way decides how many compounds can be formed by any two or more elements. This at present can only be learned by experiment, but we are not without indications that a time approaches when this further problem will receive a theoretical solution.

27 Although the atomic theory satisfactorily co-ordinates all the known laws of chemical combination, the actual existence of atoms is far from being positively proved;[1] indeed, to many

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[1] Williamson, "On the Atomic Theory," *Journ Chem. Soc.* (1869), **22,** 328 and 433.

minds it appears that the problem is by its nature incapable of solution. Nevertheless, there is evidence connected with certain physical phenomena, which strongly points to the existence of a limit to the divisibility of matter.[1] The phenomena in question belong to the science of molecular physics, and have reference to such subjects as the capillary attraction of liquids, the diffusion of gases, and the production of electricity by the contact of metals. Reasoning from facts observed in the study of these subjects, physicists have not only come to the conclusion that matter is discontinuous, and, therefore, that indivisible particles or molecules (*molecula*, a small mass) exist, but they have even gone so far as to indicate the order of magnitude which these molecules attain. Thus Lord Kelvin (Sir William Thomson) states that in any ordinary liquid or transparent or seemingly opaque solid, the mean distance between the centres of contiguous molecules is less than the one hundred-millionth, and greater than the two thousand-millionth of a centimetre. Or, in order to form a conception of this coarse-grainedness, we may imagine a rain-drop or a globe of glass as large as a pea to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion; the magnified structure would be coarser-grained than a heap of small shot, but probably less coarse-grained than a heap of cricket-balls.[2]

The molecular constitution of matter is likewise an essential condition of the mechanical theory of gases, by means of which nearly every known mechanical property of the gases can be explained on dynamical principles, so that in this direction again we have a strong suggestion of the existence of molecules (p. 85).

28 It will be seen that the atomic theory as proposed by Dalton does not provide any means for ascertaining what the relative weights of the atoms really are. We have seen, for instance, that 7·94 parts by weight of oxygen combine with one part of hydrogen to form water, but we cannot draw any conclusion from this fact as to the atomic weight of oxygen, (that of hydrogen being taken as equal to one), until we know how many atoms of each of these elements have taken part in the combination. If the combination is between an equal number of atoms of each element, then the relative weights of their atoms must be as 1 : 7·94, whilst if two atoms of hydrogen have combined with one

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[1] Rücker, *British Assoc.*, 1901.

[2] *Nature*, March 31, 1870.

of oxygen the relation will be as 1 : 15·88. The answer to this question—as to the number of atoms of each element between which combination has taken place—has been supplied by a study of the laws of combination of gaseous substances.

COMBINATION BY VOLUME.

29 The discovery by Gay-Lussac and Humboldt in 1805 of the simple relation existing between the *combining volumes* of oxygen and hydrogen gases, followed by that of the general law of gaseous volumes enunciated in 1808 by Gay-Lussac alone, serves as a powerful argument in favour of Dalton's Atomic Theory. This law states that *the volumes in which gaseous substances combine bear a simple relation to one another and to the volume of the resulting product.* This is true both for elementary and compound gases, the simple relations which exist being illustrated by the following table:

1 vol. of chlorine and 1 vol. of hydrogen form 2 vols. of hydrochloric acid gas.
1 vol. of oxygen and 2 vols. of hydrogen form 2 vols. of steam.
1 vol. of nitrogen and 3 vols. of hydrogen form 2 vols. of ammonia.
1 vol. of oxygen and 2 vols. of carbonic oxide form 2 vols. of carbon dioxide.

According to the atomic theory, however, combination takes place between the atoms of which substances are made up, and it hence follows, if we accept this theory, that *the number of atoms which is contained in a given volume of any gaseous body, must stand in a simple relation to that contained in the same volume of any other gas* (measured under equal circumstances of temperature and pressure). The simplest as well as the most probable supposition respecting this question is that put forward by Avogadro in 1811,[1] who assumed that *equal volumes of all the different gases, both elementary and compound, contain the same number of particles or molecules,* and this theory is now generally accepted by physicists, who have arrived at the same conclusion as the chemists have reached by an independent train of reasoning (p. 87). If we take the simplest case of volume combination, that of one volume (one molecule) of chlorine and one volume (one molecule) of hydrogen uniting to form two volumes (two molecules) of hydrochloric acid gas, it is

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[1] *Journ. de Phys.*, par De la Métherie, Juillet, 1811, **73**, 58–76. *Ibid.*, Feb. 1814.

clear that, since each molecule of hydrochloric acid contains at least one atom of chlorine and one of hydrogen, there are at least twice as many atoms as molecules of these elements present. Hence, to conform to Avogadro's theory, the molecule of free chlorine and of free hydrogen must consist of at least two atoms combined together, and we shall represent the combination as taking place between one volume (one molecule of two atoms) of chlorine and one volume (one molecule of two atoms) of hydrogen, forming two volumes (two molecules) of the compound hydrochloric acid gas. Again, two volumes of steam are formed from two volumes of hydrogen and one volume of oxygen, hence if there are the same number of molecules of steam, of hydrogen, and of oxygen in the same volume of each gas, it is clear that in the formation of water from its elements, each molecule of oxygen must be split up into two similar parts. We are thus led to distinguish between the *atom* and the *molecule*, the latter term being applied to *the smallest particle of an element or compound which can exist in the free state.* Avogadro's theory refers exclusively to these molecules and states *that equal volumes of all gases, measured under the same physical conditions, contain equal numbers of molecules.*

An immediate consequence of this theory is of the utmost importance. If we weigh equal volumes of two gases, we are obviously weighing equal numbers of their molecules, and the ratio of the weights of the gases will also be the ratio of the weights of their molecules, so that we are thus enabled to determine the relative weights of the molecules of all gases, by simply finding their relative densities. Hydrogen gas is taken as the standard of comparison because it has a lower density than any other gas, and, since it has been shown that its molecule can be divided into at least two parts, the weight of its molecule is taken as equal to two. *The molecular weight of any gas is therefore equal to twice its density compared with hydrogen;* nitrogen, for example, is about 14 times as heavy as hydrogen and hence its molecular weight is about 28, whilst carbon dioxide has a density of about 22 and therefore a molecular weight of about 44.

30 When the molecular weight of a gas and also its composition, as determined by analysis, are both known, it is possible to calculate what proportion of each of the component elements is present in the molecule. Water for instance contains 88·81 per cent. of oxygen and 11·19 of hydrogen, whilst the density of

steam is about 8·94, its molecular weight being, therefore, equal to 17·88. If now we calculate how much oxygen and hydrogen are present in 17·88 parts of water, we find that this amount is made up of 15·88 of oxygen and 2 of hydrogen. Carbon dioxide again has a molecular weight of 43·7, and contains

Carbon	27·27
Oxygen	72·73
	100·00

Hence 43·7 parts of this gas contain 11·91 of carbon and 31·76 of oxygen.

A repetition of this process for all the known compounds of some particular element enables us to ascertain *the least amount of that element which is ever found in a molecule of a substance*, and to this amount the name of *atom* is given.[1] A comparison of all the substances containing oxygen, for example, teaches us that the least amount of it ever found in a molecule is 15·88 parts, and this is, therefore, taken as the atomic weight of oxygen. This having been ascertained, we are in a position to say that the molecule of water contains one atom of oxygen, whilst that of carbon dioxide contains two. All the non-metallic elements, except those of the helium group, form compounds which can exist in the state of gas, and hence the atomic weights of all these elements have been found by this method. Many of the metals on the other hand do not form volatile compounds, and the atomic weights of these have, therefore, to be determined by different methods, a discussion of which will be found in a later volume (Vol. II. (1897), p. 13). In any case it must be remembered that the method described above is not generally capable of great accuracy and only yields an approximate number for the atomic weight, the exact value being found by determining the equivalent of the element by an accurate analysis of one of its compounds, and then taking as the exact atomic weight the multiple of this number which approaches most closely to the approximate number obtained from the molecular weights.

31 A few years ago the proposition was made to adopt oxygen

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[1] An atom may also be defined as "the least amount of an element which is capable of being added to or taken from a molecule of any substance."

as the standard of the atomic weights, the atomic weight of the latter being taken as 16. The reason for the proposed change was that in almost every case the actual ratio experimentally determined is that of the element in question to oxygen, the ratio to hydrogen being then calculated from the ratio of hydrogen to oxygen. As the latter is one of which the different experimental determinations were not very concordant, it was suggested that it would be better to fix the atomic weight of oxygen arbitrarily as 16, and calculate the other atomic weights on this basis, the only atomic weight then requiring alteration in case of a revision of the O : H ratio being that of hydrogen itself.[1]

Since this proposition was made (1888), the ratio of the atomic weights of hydrogen and oxygen has been carefully determined by several investigators with agreeing results, and in this book, therefore, hydrogen has been kept as the standard and unit, all other atomic weights being calculated from the ratio $O : H = 15·88 : 1$, found by the recent experiments. As, however, many chemists still prefer to take as the standard $O = 16$, the atomic weights according to both systems are shown in the table (p. 56).

32 It will be seen that the determination of the atomic weight is quite distinct from that of the molecular weight. This is well shown in the case of carbon; a comparison of the gaseous compounds of carbon shows that the *atomic weight* of this element is about 12, this being the least amount of it which is found in the molecule of one of its compounds; we are, however, quite ignorant of the *molecular weight* of carbon itself, since its density in the state of gas has never been determined.

The molecules of some elements contain as many as four atoms (phosphorus and arsenic), others contain only two atoms, this being the case with hydrogen, oxygen, nitrogen, chlorine and others, whilst the molecules of the gases of the Argon group, of mercury vapour and of the vapours of some of the other metals consist of single atoms, the molecular and atomic weights being, therefore, identical.

33 For the first time we may now employ *chemical symbols*, a kind of shorthand, by which we can conveniently express the various chemical changes. To each element we give a symbol, usually the first letter of the Latin, which is generally also that of the English name. Thus O stands for oxygen;

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[1] See Ber. 1889, **22**, 872, 1021, 1721; *Journ. Chem. Soc.* 1893, 54.

H for hydrogen; S for sulphur; Au for gold (aurum); Ag for silver (argentum). These letters, however, signify more than that a particular substance takes part in the reaction. They serve also to give the quantity by weight in which it is present. Thus O does not stand for *any* quantity, but for 15·88 parts by weight (the atomic weight) of oxygen; H always stands for one part of weight of hydrogen; and in like manner S, Au, and Ag stand invariably for 31·83, 195·7, and 107·12 parts by weight of the several elements respectively. By placing symbols of any elements side by side, a combination of the elements is signified, thus:—

HCl Hydrochloric acid.	HI Hydriodic acid.
HBr Hydrobromic acid.	HgO Mercuric oxide.

If the molecule contains more than one atom of any element, this is indicated by placing a small number below the symbol of the atom of the element, thus H_2O signifies 17·88 parts by weight of a compound (water) containing two atoms or 2 parts by weight of hydrogen and one atom or 15·88 parts by weight of oxygen. In such a case as this, where the molecular weight and the number of atoms in the molecule are known and expressed in the formula, the latter is said to be a *molecular formula* and consequently represents such a weight of the substance as will in the state of gas occupy the same volume as two parts by weight of hydrogen. When the molecular weight of the compound to be represented by a formula is not known, it is only possible to express the relative number of the atoms of the constituent elements which are present. A formula of this kind is known as an *empirical formula* and may be calculated for any substance of which the composition has been determined by analysis.

The gas known as ethylene has the following composition as determined by analysis:—

Carbon . . .	85·62
Hydrogen . .	14·38
	100·00

In order to find the empirical formula of this substance it is only necessary to divide the percentage of each element by the atomic weight of the element, which gives us the ratio of the number of atoms of each of the two elements, and if we express this ratio in the smallest possible whole numbers we have at once the relative numbers of atoms present in the molecule, without, however, having any information as to the absolute number.

	Percentage.	$\frac{\text{Percentage}}{\text{Atomic Weight.}}$	Simplest Ratio.
Carbon	85·62	7·19	1
Hydrogen . . .	14·38	14·38	2

The simplest or empirical formula of ethylene is therefore CH_2. The density of this gas however is found to be equal to 13·91 and its molecular weight is therefore 27·82, its molecular formula being consequently C_2H_4.

It is usual to represent chemical changes in the form of equations; the materials taking part in the change being placed on one side and the products formed, which are always equal to them in weight (p. 54), being placed on the other. If we heat potassium chlorate, a substance which has the empirical formula $KClO_3$, it is decomposed into oxygen and potassium chloride and this decomposition is represented by the equation

$$2KClO_3 = 2KCl + 3O_2$$

in which the sign + connects the two products and signifies "together with." This equation is an expression of the fact, ascertained by experiment, that $243·36 = (38·86 + 35·18 + 3 \times 15·88) \times 2$ parts of this salt by weight leave behind on heating 148·08 parts $= (35·18 + 38·86) \times 2$ of potassium chloride and liberate 95·28 parts of oxygen. Hence it is clear that the quantity of oxygen which is obtained from any other weight of the salt and *vice versâ* can be found by a simple calculation when the equation representing the chemical change is known.

To take a more complicated case, when we know that the equation representing the change which occurs when we heat potassium ferrocyanide, the empirical formula of which is $K_4C_6N_6Fe$, with strong sulphuric acid, H_2SO_4, and water, is the following:—

$$K_4C_6N_6Fe + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4$$

yielding carbon monoxide gas CO, potassium sulphate K_2SO_4, ammonium sulphate $(NH_4)_2SO_4$, and iron sulphate $FeSO_4$, we can easily calculate how many grams of carbon monoxide gas, CO, can be obtained from any given weight of the ferrocyanide, $K_4C_6N_6Fe$, inasmuch as analysis proves that the amounts represented by these formulæ are made up as follows:—

Carbon Monoxide.		
Carbon	C	11·91
Oxygen	O	15·88
		27·79

Ferrocyanide of Potassium.		
Potassium	K_4	155·44
Carbon	C_6	71·46
Nitrogen	N_6	83·58
Iron	Fe	55·50
		365·98

The foregoing equation then shows that 365·98 parts by weight of the ferrocyanide yield 166·74 parts by weight of carbon monoxide, and hence a simple proportion gives the quantity yielded by any other weight. The illustration is, however, not yet complete; commercial potassium ferrocyanide contains, as do many crystalline compounds, a certain quantity of *water of crystallisation*, which is given off when the salt is heated, in consequence of which the crystals fall to a powder. But, as the equation shows, a certain quantity of water takes part in the reaction, and it is, therefore, unnecessary to dry the salt previously if only we know how much water of crystallisation it contains. Analysis has shown that the commercial salt has the composition $K_4C_6N_6Fe+3H_2O$; hence if we add 3×17·88, the weight of 3 molecules of water, to 365·98, we obtain the number 419·62 as the weight of the *hydrated* salt which must be taken in order to obtain 166·74 parts by weight of carbon monoxide.

As, however, the quantity of a gas is almost always estimated by measuring its volume, and from this volume calculating its weight, it becomes of the greatest importance to know how to calculate the volume of a gas from its weight, or *vice versâ*. This can only be effected with strict accuracy by employing in each case the density of the gas as determined by experiment. An approximate number, which it is often useful to know, can however be readily obtained, since we know that *molecular proportions of all gases occupy equal volumes under the same physical conditions* (Avogadro).

Now 1 litre of hydrogen at 0°C. and 760 mm. pressure (which are generally taken as the standard temperature and pressure) weighs 0·089901 gram (Morley), and hence the volume occupied by 2 grams, or 1 gram-molecule of the gas is 2/0·089901 = 22·247 litres. The gram-molecule of every other gas therefore occupies approximately this same volume, or in other words *the molecular volume of all gases is* 22·247 *litres* (at 0°C. and 760 mm.).

The volume at the standard temperature and pressure of any weight of gas can then readily be calculated; thus 27·79 grams of carbon monoxide occupy 22·247 litres, and hence 166·74 grams occupy $\frac{22{\cdot}247 \times 166{\cdot}74}{27{\cdot}79}$ litres at 0°C. and 760 mm.

It is now easy to calculate what volume this weight will occupy at any other temperature or pressure, for we know that all gases expand by $\frac{1}{273}$ of their volume at 0°C. when their temperature is raised 1°C. at constant pressure (Law of Dalton, p. 84), and that their volume is inversely proportional to the pressure to which they are subjected (Law of Boyle, p. 83). Hence if the temperature at which the gas was collected were 17°C., and if the barometer then stood at 750 mm., the volume (v) in litres of the carbon monoxide collected would be $v = \frac{22{\cdot}247 \times 166{\cdot}74 \times (273 + 17) \times 760}{27{\cdot}79 \times 273 \times 750.}$.

DISSOCIATION.

34 In many cases it is found that the relative density of a gas, or of the vapour of some liquid or solid substance, as ascertained by experiment (p. 124), alters with the temperature at which the determination is carried out. Iodine vapour, for example, is found to have a constant density of about 126 between the temperatures of 400—700° C., and its molecular weight then corresponds with the formula I_2. Above this temperature, however, the density is found to diminish gradually, until at about 1,500° it again becomes constant at about 63, almost exactly half of its previous value. We must, therefore, assume that the molecule of iodine (I_2) is decomposed at temperatures above 700°, a gradually increasing number of its molecules being broken up as the temperature rises, until finally at 1,500° nearly all the molecules have been broken up into free atoms, each of which must now be considered as a separate molecule, the molecular weight of iodine at these high temperatures being

126, and its formula I, the change being represented by the equation:

$$\underset{1\ \text{vol.}}{I_2} = \underset{1\ \text{vol.}}{I} + \underset{1\ \text{vol.}}{I.}$$

A decomposition of this kind is known as *dissociation*. It must be remembered that in order to prove conclusively that a substance exists in the state of vapour with a definite molecular weight, the vapour density must be found to be constant throughout a considerable range of temperature. Thus, iodine vapour has a constant density between the temperatures 400—700°, and only begins to dissociate above the latter temperature. Sulphur vapour on the other hand at a temperature near its boiling-point has a relative density of 96, corresponding with the formula S_6; but this density is not constant for any definite range of temperature but gradually decreases until it reaches the value of 32 (S_2) at a temperature of 800°, above which it remains constant. In the case of iodine vapour, therefore, we have good evidence that molecules of the formula I_2 exist, whereas for the existence of sulphur molecules containing six atoms the evidence is by no means so conclusive, although it is believed by some that these exist at low temperatures (see Sulphur).

35 Frequently a compound which exists in the solid or liquid state cannot be converted into vapour without undergoing dissociation. Thus ammonia and hydrochloric acid unite directly to form ammonium chloride:

$$NH_3 + HCl = NH_4Cl.$$

Phosphorus trichloride absorbs two atoms of chlorine, and is converted into the pentachloride, thus:—

$$PCl_3 + Cl_2 = PCl_5.$$

These compounds, however, only exist in the solid or liquid state; when they are heated they decompose into the two molecules from which they have been formed.[1] In some cases this decomposition can be readily seen; thus antimony pentachloride, $SbCl_5$, decomposes into the trichloride, $SbCl_3$, and free chlorine. Other compounds, such as pentachloride of phosphorus, PCl_5, appear to volatilise without decomposition, but in this case it can be proved that the vapour is a mixture, and contains the

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[1] When very thoroughly dried, ammonium chloride can be vaporised without being dissociated.

molecules of two gases, phosphorus trichloride, PCl_3, and free chlorine. The vapour densities of these bodies accordingly do not follow the usual law; thus the vapour of chloride of ammonium, if it consisted of similar molecules, must possess the density of $\frac{35{\cdot}18+13{\cdot}93+4}{2}=26{\cdot}56$. In fact, however, its density is only half this number, for two volumes contain one volume of ammonia and one of hydrochloric acid; hence its density (or the weight of one volume) is half the above or 13·28.

In the same way iodine forms both a monochloride ICl and a trichloride ICl_3: the first of these bodies is volatile without decomposition; the second, however, decomposes on distillation into the molecules ICl and Cl_2.

PROPERTIES OF GASES.

36 The chemist has to deal with matter in all its various states; solids, liquids, and gases alike being the objects of his examination. The study of gases in particular has, as we have seen, led to most important results in the theoretical branch of the science, the system of formulæ now employed being in fact founded upon observations made upon matter in the state of gas.

RELATION OF VOLUME TO PRESSURE. BOYLE'S LAW.

37 The gaseous condition of matter is well defined to be that in which it is capable of indefinite expansion. If a quantity of gas as small as we please be placed in a closed vacuous space, however large, the gas will distribute itself uniformly throughout that space. The relation between the volume and pressure of a gas, the temperature remaining constant, is expressed by the well-known law of Boyle (1662), viz., that *the volume of the gas varies inversely as the pressure*, from which it follows that the product of pressure and volume remains constant whatever be the pressure. This is expressed by the equation $PV=C$; thus when the pressure is doubled, the volume is halved, the product of the two remaining the same. When a number of gases which do not act chemically on each other are mixed together, the total pressure exerted is equal to the sum

of the separate pressures which each gas would exert if it alone occupied the whole space, or as it may be otherwise expressed, the total pressure of a mixture of gases is equal to the sum of the partial pressures of its constituent gases (Dalton).

Thus, if a litre of oxygen at a pressure of 0·2 of an atmosphere and a litre of nitrogen at a pressure of 0·8 of an atmosphere be mixed and the volume again brought to 1 litre, the total pressure will be 1 atmosphere, this being the sum of the partial pressures of the oxygen and nitrogen.

38 The adoption of the pressure of a column of mercury 760 mm. high as the normal or standard pressure leads to the anomaly that the mass of a given volume of gas, under standard conditions, varies at different places on the earth's surface, since the pressure exerted by a column of 760 mm. of mercury varies with the latitude and the height above sea level, owing to the variation in the intensity of gravitation. Hence when the weight of a given volume is quoted the locality for which it has been determined must also be stated. One litre of oxygen at 0° and 760 mm. pressure for example weighs 1·42900 grams at sea level in latitude 45°, whereas at Paris it weighs 1·42945 grams. As a rule such weights are quoted for Paris.

Relation of Volume to Temperature. Dalton's Law.

39 Another simple numerical law, which characterises the gaseous condition, is known as the law of Dalton,[1] but often referred to as the law of Charles or of Gay-Lussac.[2] This states that all gases heated under constant pressure expand by an equal fraction of their volume at 0° Centigrade for equal increments of temperature, one volume at 0° becoming 1·3665 at 100°; so that the coefficient of expansion of gases is 0·003665 or nearly $\frac{1}{273}$ for an increase from 0° to 1° Centigrade. If the temperature of the gas be lowered, the volume contracts in the same proportion. When, on the other hand, the volume of a gas is kept constant and the temperature raised, the pressure of the gas increases in this same ratio; so that a mass of gas

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[1] Dalton, *Manchester Memoirs*, v. 535 (1801).

[2] The experiments of Gay-Lussac were published at a later date than those of Dalton. The results obtained by Charles were never published, but were verbally communicated to Gay-Lussac. Gay-Lussac, *Ann. Chim.* [1], 43, 137. Dixon, *Memoirs Lit. and Phil. Soc. of Manchester* [4], **4**, 36.

which at 0° has a pressure of 1, has at 100° a pressure of 1·3665 if it be not allowed to increase in volume.

If a gas when cooled continued to follow this law, its volume would become zero at a temperature of 1/0·003665 or about −273°C. This temperature is, therefore, known as the absolute zero and temperatures reckoned from it are termed absolute temperatures. The law of expansion of gases at constant pressure may then be expressed in the simple form that the volume of a gas is proportional to the absolute temperature, or expressed in symbols $V = KT$.

Combining this equation with that previously given for the relation of pressure and volume, we obtain an expression, known as the gas equation, which embodies the relations of pressure (P), volume (V), and absolute temperature (T) for all gases:

$$PV = RT.$$

where R is a constant depending on the mass of gas taken. If V be taken as 22·247 litres (p. 81), and a corresponding value be given to R, the equation becomes at once applicable to the gram-molecule of all gases, since the molecular volume of all gases is the same (Avogadro).

40 The laws of Boyle and Dalton do not hold strictly for all gases, and the deviations from them are in some cases considerable: these are discussed on p. 96.

THE KINETIC THEORY OF GASES.

41 The behaviour of substances in the gaseous state as regards pressure and temperature is distinguished by its simplicity and uniformity from that of the solid and liquid forms of matter. For in the case of solids and liquids the effect on the volume of alteration of pressure as well as of temperature is different for every substance, whilst gases are all uniformly affected. Hence we are led to conclude that the gaseous form of matter is that in which the constitution is most simple, and this result is borne out by many other considerations.

The doctrine that heat is only a mode of motion is one which is now generally admitted, so that a hot body may be regarded as possessing a store of energy, some portion of which at any rate may be made use of to accomplish actual work. The energy of motion is termed Kinetic (from *κινέω*, I move), and this energy is communicated when the body possessing it comes to rest by contact with some other body. The other form of energy depending on position with respect to other bodies and not upon the condition of matter is termed Potential energy. It has been shown that in a hot body a very considerable portion of the energy arises from a motion of the parts of the body; so that every hot body is in motion, but this motion is not one affecting the motion of the mass as a whole but only that of the molecules or small portions of the body. These molecules may consist of a collection or system of smaller parts or atoms which partake as a whole of this general motion of the molecule. The subject of the motion of the smallest particles of matter attracted the attention of the ancients, and Lucretius held that the different properties of matter depended upon such a motion. Daniel Bernoulli was the first to conceive the idea that the pressure of the air could be explained by the impact of its particles on the walls of the containing vessel, whilst in the year 1848, Joule[1] showed that these views were correct, and calculated the mean velocity which the molecules must possess in order to bring about the observed pressure. Since the above date, Clausius, Maxwell, and other physicists have extended and completed the dynamical theory of gases. Many of the phenomena observed in gases and also in liquids, especially diffusion, prove that the large number of small particles or molecules of which these forms of matter are made up are in a constant condition of change or agitation, and the hotter a body is the greater is the amount of this agitation. According to the kinetic theory these molecules are supposed to move with great velocity amongst one another, and, when not otherwise acted on by external forces, this motion is a rectilinear one, and the velocity uniform. The molecules, however, come into frequent "collision" with one another, or, as Maxwell describes it, encounters between two molecules occur. In these encounters, and also when the molecules strike the surface of the containing vessel, no loss of energy takes place, provided of course that everything is at the same temperature, so that the total energy of the enclosed system remains unaltered.

42 From these principles, assuming simply that the molecules have weight and are in motion, and applying the usual laws of

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[1] *Brit. Assoc. Reports*, 1848, 2nd Part, p. 21.

masses in motion, the experimental laws of gases, already alluded to, as well as others, may be deduced. The pressure of a gas is thus due to the impacts of its molecules upon the walls of the containing vessel; hence, when twice as many molecules are crowded into a given space, by the compression of the gas to half of its original volume, the frequency of the impacts, and, therefore, also the resulting pressure, will be doubled, or, in other words, the pressure is inversely proportional to the volume (Boyle's Law). The temperature is measured by the kinetic energy of the molecules, which is equal to the product of half their mass into the square of their velocity, *i.e.*, $\frac{1}{2} mv^2$. Increase of temperature, therefore, means increase of the velocities of the molecules, and hence if the volume of a gas be kept constant and its temperature raised, both the force of impact of each molecule against the wall of the vessel and the number of impacts per second will be increased, the pressure rising in proportion to the square of the velocity, or in other words in direct proportion to the rise of temperature (Dalton's Law). The temperature at which the velocity of the molecules, and, therefore, also the kinetic energy, would become equal to nothing, is the absolute zero of temperature (p. 85).

When two gases are at the same pressure, the total kinetic energy of the molecules in equal volumes must be the same; if their temperatures are also equal, the mean kinetic energy of each molecule must also be equal, and it hence follows that the number of molecules in equal volumes of the two gases must be the same. Assuming then that the temperature of a gas represents the kinetic energy of its molecules it follows that equal volumes of all gases under similar conditions of temperature and pressure contain equal numbers of molecules. This is the statement known to chemists as Avogadro's theory (p. 74), which is thus shown to rest upon a sound physical foundation.

43 The velocities of the molecules can be calculated for any given temperature when we know the density of the gas and its pressure at that temperature. As will be seen from the table given below their magnitude is very considerable, and this accounts for the great velocity with which disturbances, such as sound waves or explosions, are propagated through gases.

	Velocity at 0° in metres per second.
Hydrogen	1,838
Ammonia	628
Oxygen	461
Carbon dioxide	392
Chlorine	310
Hydriodic acid	230

These numbers represent the mean velocity of the molecules, since it is supposed that owing to encounters the velocity is not absolutely uniform but varies about an average value; in hydrogen for example at 0° C. and 760 mm. some of the molecules are moving at a much slower rate than 1,838 metres per second, while others are moving much more rapidly. In addition to the energy of translation which the molecule as a whole possesses, the atoms of which it is composed and which are capable of motion relatively to each other have also a certain amount of kinetic energy. When a gas is heated, therefore, both of these kinds of energy are increased, or in other words the motion of the atoms within the molecule is increased at the same time as the velocity of the molecule itself.

Clerk-Maxwell and others have calculated that the actual number of molecules which we must conclude to be present in one cubic centimetre of a gas at the standard temperature and pressure is no less than 21 trillions (21,000,000,000,000,000,000 or 21×10^{18}); the weight of a single molecule of hydrogen being, therefore, about 0·000 000 000 000 000 000 04 milligrams or ($0{\cdot}04 \times 10^{-18}$).

In spite of the high speed of a molecule of a gas it only moves freely for a very short distance before it comes into "collision" with another molecule, and it has been calculated from experiments on the viscosity of gases that the mean "free path" of a molecule of hydrogen, the most rapidly moving of all the gases, is at 0° and 760 mm. only 0·0000178 ($17{\cdot}8 \times 10^{-6}$) mm., whilst it experiences 9,520 million collisions with other molecules per second. The corresponding numbers for oxygen are 0·0000102 ($10{\cdot}2 \times 10^{-6}$) mm. and 4,180 million, and for carbon dioxide 0·0000065 ($6{\cdot}5 \times 10^{-6}$) mm. and 5,530 million collisions per second.[1]

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[1] Quoted from O. E. Meyer, *Kinetic Theory of Gases* (London, 1899), p. 192.

DIFFUSION OF GASES.

44 Early in the history of the chemistry of gases it was observed that when gases of different specific gravities, which exert no mutual chemical action, are once thoroughly mixed they do not of themselves separate in the order of their several densities by long standing. On the contrary, they remain uniformly distributed throughout the mass. Priestley[1] proved this by very satisfactory experiments; but he believed that if the different gases were very carefully brought together, the heavier one being placed beneath and the lighter one being brought on to the top without being mixed with the other, they would then, on being allowed to stand, not mix but continue separate one above the other. Dalton,[2] in 1803, proceeded to investigate this point, and he came to the conclusion that a lighter gas cannot rest upon a heavier, as oil upon water, but that the particles of the two gases are constantly diffusing through each other until an equilibrium is reached, and this without any regard to their specific gravities. This conclusion Dalton regarded as a necessary consequence of his theory of the constitution of matter, according to which the particles of all gaseous bodies exert a repulsive influence on each other, and each gas expands into the space occupied by the other as it would into a vacuum. In fact, however, it does not so expand, for the rate at which a gas diffuses into another gas is many thousand times slower than that at which it rushes into a vacuum.[3] As was usual with him, the apparatus used by Dalton in these experiments was of the simplest kind. It consisted of a few phials and tubes with perforated corks. "The tube mostly used was one 10 inches long and of $\frac{1}{20}$ inch bore; in some cases a tube of 30 inches in length and $\frac{1}{3}$ inch bore was used; the phials held the gases which were the subject of experiment and the tube formed the connection. In all cases the heavier gas was in the lower phial and the two were placed in a perpendicular position, and suffered to remain so during the experiment in a state of rest; thus circumstanced it is evident that the effect of agitation was sufficiently guarded against; for a tube almost capillary and 10 inches long, could not be instrumental in propagating an intermixture from a momentary com-

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[1] *Observations on Air*, **2**, 441.

[2] *Manch. Memoirs*, 1805, p. 259.

[3] *Phil. Mag.* 1863 [4], **26**, 409.

motion at the commencement of each experiment." The gases experimented on were atmospheric air, oxygen, hydrogen, nitrogen, nitrous oxide, and carbonic acid; and after the gases had remained in contact for a certain length of time the composition of that contained in each phial was determined, and invariably showed that a passage of the heavier gas upwards and the lighter gas downwards had occurred. Similar experimental results were also obtained by Berthollet in 1809.[1]

The passage of gases through fine pores was likewise observed by Priestley [2] in the case of unglazed earthenware retorts which, although perfectly air-tight so as not to allow of any escape by blowing in, allowed the vapour of water to pass out whilst air came in, even where the gas in the retort was under a greater pressure than that outside. Dalton was the first to explain this fact as being due to precisely the same cause as that which brings about the exchange of gases in the phials connected with the long tubes, only that here we have a large number of small pores instead of one (the bore of the tube) of sensible magnitude.

In the year 1823 Döbereiner[3] made the remarkable observation that hydrogen gas collected over water in a large flask which happened to have a fine crack in the glass, escaped through the crack into the air, whilst the level of the water rose in the flask to a height of nearly three inches above its level in the trough. Air placed in the same flask did not produce a similar effect, nor was this rise of the water observed with the flask full of hydrogen when it was surrounded with a bell-jar filled with the same gas.

45 As in the former instance, the discoverer of the fact was unable to explain the phenomenon, and it was not until 1832 that Thomas Graham [4] in repeating Döbereiner's experiments showed that no hydrogen could escape by the crack without some air coming in, and enunciated the law of gaseous diffusion founded on the results of his experiments, viz., that the rate at which gases diffuse is not the same for all gases but that their *relative rates of diffusion are inversely proportional to the square roots of their densities*, so that hydrogen and oxygen having the relation of their densities as 1 to 16 the relative rates of diffusion are as 4 to 1.

Instead of using cracked vessels Graham employed a *diffusion*

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[1] *Mém. d'Arcueil*, **2**, 463.

[2] *Observations, &c.*, **2**, 414.

[3] *Ann. Chim. Phys.* 1823, **24**, 332.

[4] *Edin. Phil. Trans.* 1834, **12**, 222. *Phil. Mag.* 1833, **2**, 175.

tube consisting of a glass tube open at each end and about six to fourteen inches in length and half an inch in diameter; a wooden cylinder is introduced into the tube so as to fill it with the exception of a short space at one end, and this unoccupied space is filled with a plug of plaster of Paris, the cylinder being withdrawn after the paste of plaster has set. With such a tube divided into volumes of capacity, filled with gas and placed over water, the rate of the rise or depression of the water could be easily observed and the composition of the gas both before and after the experiment ascertained. In this way the relative diffusibility of various gases was determined, the results of Graham's experiments being shown in the following table.

DIFFUSION OF GASES.

Gas.	Density.	Square root of density.	$\frac{1}{\sqrt{\text{density}}}$	Velocity of diffusion. Air = 1.
Hydrogen	0·06949	0·2636	3·7935	3·83
Marsh gas	0·559	0·7476	1·3375	1·344
Steam	0·6235	0·7896	1·2664	—
Carbonic oxide	0·9678	0·9837	1·0165	1·1149
Nitrogen	0·9713	0·9856	1·0147	1·0143
Ethylene	0·978	0·9889	1·0112	1·0191
Nitric oxide	1·039	1·0196	0·9808	—
Oxygen	1·1056	1·0515	0·9510	0·9487
Sulphuretted hydrogen .	1·1912	1·0914	0·9162	0·95
Nitrous oxide	1·527	1·2357	0·8092	0·82
Carbon dioxide	1·52901	1·2365	0·8087	0·812
Sulphurous acid . . .	2·247	1·4991	0·6671	0·68

The observed velocities of diffusion agree very closely with those obtained by calculation. This is, however, only the case when the porous plate through which the diffusion takes place is very thin. If the plate be thick the gases have to pass through a series of capillary tubes, and the rate of diffusion is considerably diminished by the friction.

46 The passage of the gases through capillary tubes has been termed *transpiration of gases*, and this proceeds according to other laws than those of diffusion, the velocity of the gases being greatly affected by their viscosity. Thus when allowed to pass through capillary tubes the rate of transpiration of equal volumes of the following gases was found by Graham to be represented by the numbers:—

Oxygen	1·00
Hydrogen	0·44
Carbon dioxide	0·72

These numbers bear no relation to the square roots of the densities of the gases.

47 Of all substances, that which is best adapted for exhibiting the laws of diffusion is a thin plate of artificial graphite. With a porous plate of graphite 0·5 mm. in thickness Graham[1] obtained the following times of diffusion into air under a pressure of 100 mm. of mercury:—

	Time of molecular passage.	Square root of density O = 1.
Hydrogen	0·2472	0·2509
Oxygen	1·0000	1·0000
Carbon dioxide	1·1886	1·1760

When the same gases were allowed to diffuse into a vacuum the following were the results:—

	Time of molecular passage.	Square root of density O = 1.
Hydrogen	0·2505	0·2509
Air	0·9501	0·9507
Oxygen	1·0000	1·0000
Carbon dioxide	1·1860	1·1760

Hence it appears that a plate of artificial graphite is practically impermeable to gas by transpiration but is readily penetrated by gases when in molecular or diffusive movement, whether the gases pass under pressure into air or into a vacuum, and this substance, therefore, serves as a kind of "pneumatic sieve" which permits the passage of the molecules but not the masses of the gas.

The diffusion of gases without the intervention of a porous septum has been investigated by Lohschmidt.[2] It is a complicated phenomenon in which, as in transpiration, gaseous friction plays a large part.

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[1] *Phil. Trans.* 1863, 392.

[2] *Wien. akad. Ber.* 1870, **61**, 367; **62**, 468.

48 *Effusion of Gases* is the name given by Graham to the flow of gases under pressure through a minute aperture in a thin metallic plate. The law of diffusion is found to hold good with regard to this molecular motion of gases, the times required for equal volumes of different gases to flow through an aperture of a diameter of $\frac{1}{500}$ of an inch having been found to be very nearly proportional to the square roots of their densities, and the velocity of flow to be therefore inversely as the square roots of their densities. This law, which is true for the flow of all fluids through a small aperture in a thin plate, has been applied by Bunsen[1] for the purpose of determining the specific gravity of gases, the method serving admirably when only small quantities of the gas can be obtained.

49 It will be observed that the rates of effusion and of diffusion through porous septa, as determined by Graham, are directly proportional to the molecular velocities, according to the kinetic theory of gases, which, as has already been stated, are inversely proportional to the square root of the density of the gas.

50 The phenomena of diffusion can be strikingly demonstrated by the following experiments:—

To one end of a glass tube about 1 metre in length and 1 cm. in diameter, having a bulb blown on to it, a cylindrical porous cell (such as those used for galvanic batteries) is fixed by means of a caoutchouc stopper. The other end of the tube is drawn out to a fine point and bent round as shown in Fig. 10 (p. 94). If now a vessel filled with hydrogen be held over the porous jar this gas will enter more quickly than the air can issue, viz., in the inverse proportion of the square roots of their densities, that is, as $\sqrt{14{\cdot}4}$ to 1, or as 3·8 volumes to one volume, so that the pressure in the porous cell will increase and the coloured water placed in the bulb will be driven out in the form of a fountain through the narrow jet.

A second experiment showing the mode in which one gas may be separated from another by diffusion (termed *atmolysis* from ἀτμός vapour and λύω I loosen) is the following. A slow current of the detonating gas obtained by the electrolysis of water, and consisting of two volumes of hydrogen to one volume of oxygen, is allowed to pass through a common long clay tobacco-pipe, the gas on issuing from the pipe being collected over water in a pneumatic trough. On bringing the gas, thus collected, in contact with a flame it no longer detonates. On the contrary,

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[1] *Gasometry*, 121.

it will rekindle a glowing chip of wood, thus showing that in its passage through the porous pipe the lighter hydrogen has escaped by diffusion through the pores of the clay very much more rapidly than the heavier oxygen.

Fig. 10.

A third experiment to illustrate the law of diffusion is one which possesses interest from another point of view, inasmuch as it has been proposed to employ the arrangement for giving warning of the outbreak of the dangerous and explosive gas termed fire-damp by the coal-miners. Fire-damp or marsh gas is lighter than air, and 134 volumes of this gas will diffuse through a porous medium in the same time as 100 volumes of air will do. Hence if a quantity of fire-damp surround the porous plate the volume within the vessel will become larger, and this increase of volume may be made available either to drive out water as in the first experiment or to alter the level of a column of mercury so as to make contact with a connected battery and then to ring a warning bell. The latter form of apparatus is seen in Fig. 11. Holding a beaker-glass (A) filled with hydrogen or common coal-gas over the plate of porous stucco fastened into the tube-funnel, an increase of volume occurs inside the glass tube and a consequent depression of the mercury takes place in the bend of the tube which is sufficient to make metallic contact with a second platinum wire fused through the glass and to bring the current to act on the magnet of the electric-bell (B). The other tube is arranged for showing that a dense gas, such as carbonic acid, does not diffuse through the porous septum so quickly as air escapes. By immersing the porous plate in a jar (C) filled with the heavy gas, the volume inside the tube

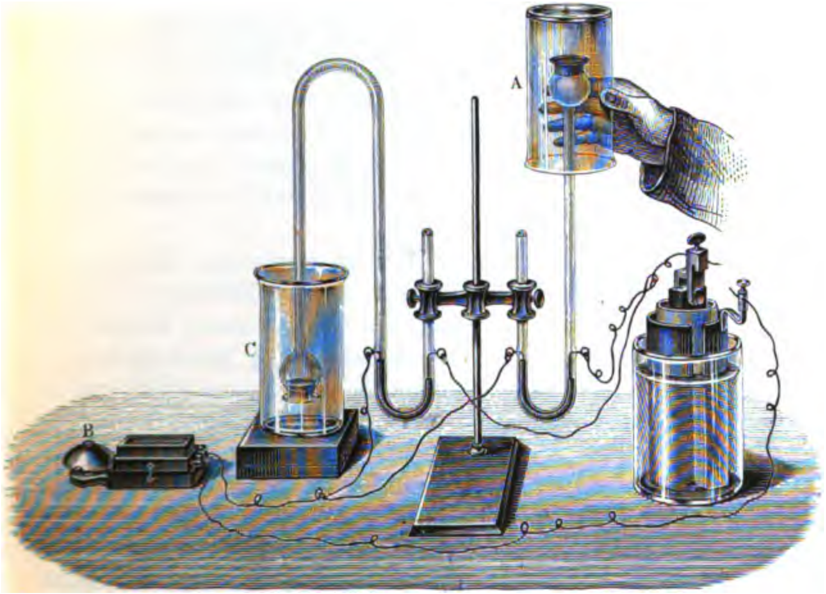

FIG. 11.

becomes less, the level of the mercury in the bend is altered, contact is again made with the battery, and the ringing of the bell gives notice of the change.

DEVIATIONS FROM THE LAWS OF BOYLE AND DALTON.

51 These laws are only approximately true, for it is found that no gas exactly follows them under all conditions of temperature and pressure, although under moderate variations of these conditions the deviations are but slight. The ideal gas which would agree with these laws under all conditions is called a perfect gas, and this term is often also applied to gases which approach this state. The effect of high pressures upon certain gases is shown in the following diagram exhibiting the experimental values obtained for the product of pressure and volume with hydrogen (A), ethylene (B), and carbon dioxide (C) at 100° (Amagat). For a perfect gas, as already mentioned, this product would remain invariable and would be represented in the diagram by a horizontal line.

Two factors seem to be involved in producing deviations of this character. In the first place, as the density of the gas increases, the volume occupied by the molecules themselves, which we must suppose to be unalterable by pressure, bears a greater proportion to the distance between them, which can be lessened by compression, and consequently the volume diminishes less rapidly than when the density is smaller, and hence pv increases. Secondly, as the molecules approach one another more closely, they tend to cohere, and the volume is thereby diminished more rapidly than the pressure increases, and hence pv diminishes. The actual effect produced is generally due to a combination of these two causes; thus the volume of carbon dioxide at a temperature of 100° (Fig. 12, C, p. 97) decreases more rapidly than we should expect from Boyle's law until a pressure of 160 atmospheres is reached, after which it decreases less rapidly, and ethylene (B) behaves in a similar manner. Hydrogen (A), however, under these conditions exhibits the preponderating influence of the first of these factors, the product of pressure and volume becoming gradually greater throughout the entire range of pressure.

The following table contains the results obtained by Amagat[1] for some of the less easily condensable gases:—

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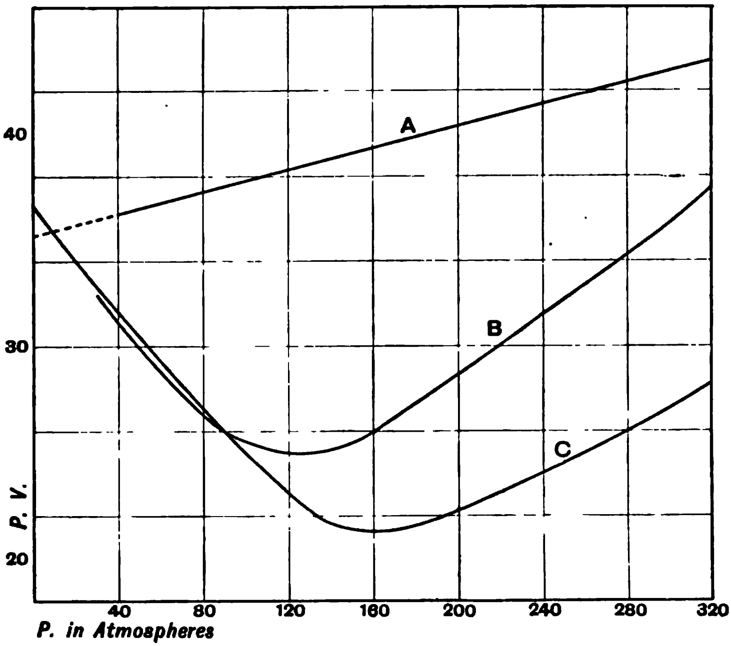
[1] *Ann. Chim. Phys.* 1893, [6], **29**, 68.

P	VALUE OF PV AT 0.		
(atmospheres).	Hydrogen.	Oxygen.	Nitrogen.
1	1·0000	1·0000	1·0000
100	1·0690	0·9265	0·9910
200	1·1380	0·9140	1·0390
300	1·2090	0·9685	1·1360
500	1·3565	1·1570	1·3900
1,000	1·7250	1·7360	2·0700
1,500	2·0700	2·2890	2·7202
2,000	2·3890	2·8160	3·3270
2,500	2·6950	3·3237	3·9200

The simple gas equation, $pv = RT$, which is only strictly applicable to a perfect gas, has been modified by Van der Waals



A Hydrogen. B Ethylene. C Carbon dioxide.

FIG. 13.

to express these deviations by the introduction of terms which allow for the influence of the two factors already discussed, and it then receives the form

$$(p+\frac{a}{v^2})(v-b)=RT,$$

where $\frac{a}{v^2}$ represents the effect of the mutual attraction of the molecules, and b represents the volume of the gas when compressed to the utmost possible extent.

By means of this equation the passage of a gas with changing temperature and pressure from the perfect state to the condition of a liquid can be calculated, when once the constants a and b have been determined from two suitable observations.

Deviations of a similar character are observed when the density of a gas is increased by lowering its temperature.

If any gas be subjected to a greatly increased pressure and its temperature simultaneously greatly reduced, a point is at last reached at which the gas undergoes sudden contraction and becomes converted into a liquid. Just before liquefaction the gas may be considered as the vapour of a liquid, so that carbon dioxide at a high pressure and a low temperature may be compared to steam just about to condense.

THE CONTINUITY OF THE GASEOUS AND LIQUID STATES OF MATTER.

52 It is matter of everyday experience that the pressure of the vapour of water and of other liquids heated with excess of the liquid in closed vessels increases in a very rapid ratio with increase of temperature, and that the density of the steam or vapour in such a case undergoes a similar rapid increase. Thus at 231° the weight of a cubic metre of steam evolved in a closed vessel in contact with water is $\frac{1}{82}$ part of the weight of the same bulk of water at 4°, the point of maximum density, the weight of steam at 100° being only $\frac{1}{1700}$ of that of the same bulk of water, so that at a temperature not very far above 230° the weight of the vapour will become equal to that of the liquid. The result of this must be that in these circumstances a change from the gaseous to the liquid state is not accompanied by any condensation, and in such a case the distinctions we have been in the habit of drawing between these conditions of matter cease to have any meaning. So long ago as 1822, Cagniard de la Tour[1] made experiments upon the action of liquids sealed up in glass tubes of a capacity but little greater than that of the liquid. When a tube one-fourth filled with

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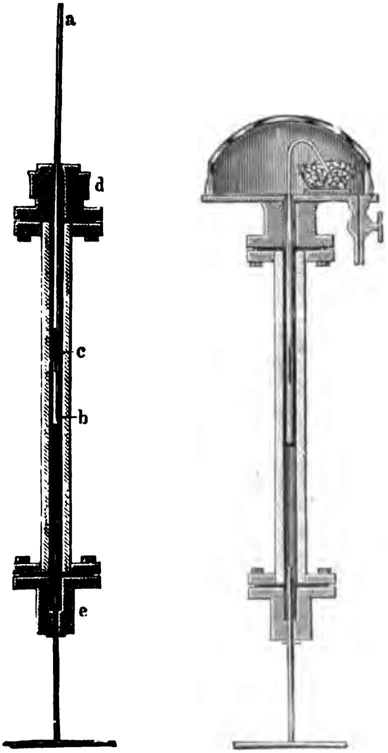
[1] *Ann. Chim. Phys.* 1823, [2], **21**, 127; **22**, 410.

water was heated to about 360°, the water entirely disappeared, the tube appearing empty, and as the vapour cooled a point was reached at which a kind of cloud made its appearance, and a few moments later the liquid was again visible. Cagniard de la Tour considered that the substance when thus heated assumes the gaseous condition; but Andrews[1] has shown that in such an experiment the properties of the liquid and those of the vapour constantly approach one another, so that above a given temperature the properties of the two states cannot be distinguished. Hence it follows that at all temperatures above this particular one no increase of pressure can bring about the change by condensation which we term liquefaction. This temperature is termed by Andrews the *critical point*, that of carbon dioxide being found by him to be 30·92°, whilst according to more recent observations it is 31·35°, the pressure at this temperature, or the *critical pressure*, being 72·9 atmospheres,[2] and the *critical volume* (or volume occupied by 1 gram of the substance at the critical temperature) 3·34 c.c., 0·0066 of the volume occupied by 1 gram at 0° and 760 mm. In order to determine this point, Andrews employed the apparatus shown in Figs. 14 and 15. The dry and pure gas is contained in the glass tube *a b*, which is closed at *a* and open at *b*, the gas being shut in by the thread of mercury *c*. This tube is firmly bedded in the brass end-piece *d*, and this, in its turn, is bolted on to the strong copper tube which carries a second end-piece



Figs. 14 and 15.

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[1] *Phil. Trans.* 1869, part ii., 575.

[2] Amagat, *Compt. Rend.* 1892, **114**, 1093.

at its lower extremity. Through this the steel screw *e* passes, packed with leather washers to render the cylinder perfectly air-tight. The cylinder is completely filled with water, and the pressure on the gas is increased up to 400 atmospheres by turning the steel screw *e* into the water. The closed and capillary end of the tube containing the compressed gas is sometimes surrounded with a cylinder into which water of a given temperature is brought. A second modification of the apparatus is shown in Fig. 15. The capillary pressure-tube is bent round so as to render it possible to place it in a freezing mixture under the receiver of an air-pump. The action both of great pressure and great cold upon the condensed gas can thus be examined.

If the screw be turned round when the gas possesses a temperature below the critical point, liquid carbon dioxide is formed when a certain pressure is reached, and a layer of this liquid can be distinctly seen lying with the gas above it. If the same experiment be repeated at a temperature above the critical one, no liquid is seen to form even when the pressure is increased to 150 atmospheres. The volume gradually diminishes, no line of demarcation or other alteration in appearance can be observed, and the tube appears as empty as it did before the gas was submitted to pressure. If the temperature be now lowered below 31·35°, the whole mass becomes liquid, and when the pressure is diminished begins to boil, two distinct layers of liquid and gaseous matter being again observed. Thus, whilst at all temperatures below 31·35° carbon dioxide gas cannot be converted into a liquid without a sudden condensation, from temperatures above this point gaseous carbon dioxide may, by the application of great pressure and subsequent cooling to below the critical point, be made to pass into a distinctly liquid condition without undergoing any sudden change such as is observed in the case of ordinary liquefaction. Precisely the same method has been applied to the determination of the critical temperatures of other gases.

The critical temperatures and pressures of a few gases and liquids along with their boiling points are given in the following table:—

	Boiling point. ° C.	Critical temperature. ° C.	Critical pressure. Atmospheres.
Hydrogen . .	−252·5	−242	15·26
Nitrogen . .	−195·5	−149	27·54
Argon . . .	−186·1	−117·4	52·89
Oxygen . .	−182·5	−119	58
Methane . .	−164·7	− 82	55·79
Ethylene . .	−103·5	+ 9	58
Carbon dioxide	− 80	+ 31·35	72·37
Ammonia . .	− 38·5	+131	113·03
Alcohol . .	+ 78·4	+243·6	62·8
Benzene . .	+ 80·3	+288·5	47·9
Water . . .	+100	+365	200·5

The critical temperature, as already pointed out, is the determining factor for the condensability of a gas, since this temperature must be reached before liquefaction can occur. As the temperature of a gas approaches the critical point, moreover, the gas deviates to a greater extent from the simple gas laws, so that in general it may be said that the lower the critical temperature of a gas, the more nearly does the gas under normal conditions approach to the ideal condition of a perfect gas.

LIQUEFACTION OF GASES.

53 The first instance of a substance, which, under ordinary conditions, is known as a gas, being transformed by pressure into a liquid is chlorine gas. This gas was first liquefied under pressure by Northmore[1] in 1806. Faraday investigated the subject fully shortly afterwards,[2] showing that many other gases, such as sulphur dioxide, carbonic acid, euchlorine, nitrous oxide, cyanogen, ammonia, and hydrochloric acid, can also be reduced to the liquid state. In these experiments Faraday employed bent tubes made of strong glass, in the one limb of which, being closed at the end, materials were placed which on being heated would yield the gas; the open limb of the tube was then hermetically sealed, and the gas evolved by heating the other end. The pressure exerted by the gas itself, when thus generated in a closed space, is sufficient to condense a portion into the liquid state. The following table shows the

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[1] Northmore, *Nicholson's Journal*, **12**, 368; **13**, 232.

[2] *Phil. Trans.* 1823, 160, 189.

maximum pressures of some of these more readily liquefiable gases at 0° :—

Table of Pressures at 0° C.

	Atmospheres.		Atmospheres.
Sulphur dioxide . .	1·53	Sulphuretted hydrogen	10·00
Cyanogen	2·37	Hydrochloric acid . .	26·20
Hydriodic acid . .	3·97	Nitrous oxide	32·00
Ammonia	4·40	Carbon dioxide . . .	38·50
Chlorine	8·95		

If, therefore, any of the above gases at 0° be exposed to pressures exceeding those given in the table they will condense to liquids, their critical temperatures being all above 0°. Sulphur dioxide, for example, can be readily liquefied in a strong glass tube fitted with a piston by the pressure exerted by the hand.

The liquefaction of gases can be brought about not merely by simple exposure to high pressure but also to low temperature;[1] thus, if we reduce the temperature of sulphur dioxide, under the ordinary atmospheric pressure, to −10° it liquefies, and when the temperature sinks to −76° the liquid freezes to an ice-like mass.

Before 1877 all the known gases had been liquefied by the application of pressure and cold, either alone or in combination, with the exception of six—hydrogen, oxygen, nitrogen, carbon monoxide, marsh gas, and nitric oxide—and to these six the name of the permanent gases was given.

The meeting of the French Academy of the 24th December, 1877, was a memorable one. On that day the Academicians were told that Cailletet[2] had succeeded in liquefying both oxygen and carbon monoxide at his works at Chatillon-sur-Seine, and that the former gas had also been liquefied by Raoul Pictet[3] at Geneva.

These experimenters soon succeeded in condensing the other gases already named, with the exception of hydrogen, which has, however, since yielded to the lower temperatures produced by later workers, and thus we are able to give experimental proof of the view which has been frequently expressed that all bodies without exception possess the power of cohesive attraction. These important results were arrived at independently by both

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[1] Faraday, *Phil. Trans.* 1845, 155.

[2] *Compt. Rend.* 1877, **85**, 815.

[3] *Compt. Rend.* 1877, **85**, 1214, 1220.

observers, each having made the question the subject of many years' study and experiment. It is difficult, on reading the description of these experiments, to know which to admire most, the ingenious and well-adapted arrangement of the apparatus employed by Pictet, or the singular simplicity of that used by Cailletet.

The process successfully adopted in each case consisted in simultaneously exposing the gas to a very high pressure and to a very low temperature.

The increase of pressure was effected by Pictet by evolving the gas in a wrought-iron vessel strong enough to withstand an enormous pressure; whilst in Cailletet's arrangement the same end was brought about by a hydraulic press. For the purpose of obtaining a low temperature the first experimenter made use of the rapid evaporation of liquid carbon dioxide, thus producing a constant temperature of −140°. Cailletet, on the other hand, effected the same end by suddenly diminishing the pressure upon the compressed gas. This sudden expansion gives rise to a rapid diminution of temperature caused by the transference of heat into the motion of the particles of the expanding gas (*chaleur de détente*) and of the mercury in the apparatus. So great is the amount of heat thus absorbed that the temperature of the particles sinks below the critical point of the gases, and a condensation occurs, the finely divided liquid oxygen or nitrogen appearing as a mist in the tube.

PICTET'S METHOD OF LIQUEFYING GASES.

54 A ground plan of Pictet's apparatus is shown in Fig. 16. The oxygen was evolved by heating potassium chlorate in a strong wrought-iron retort, *B*, connected with a copper condensation tube, *A*, four meters long, fitted with a stopcock, *V*, and a Bourdon's manometer *m'*. The reduction of temperature was brought about in two stages; in the first place, liquid sulphur dioxide was produced by the pumps, *pp'*, in the reservoir, *C*, and evaporated at −65° in the tube *R*; in the second place, carbon dioxide was liquefied by the pumps, *o o'*, in the tube *S*, which was surrounded by the sulphur dioxide evaporating in *R*, and was then allowed to flow through the jacket, *D*, surrounding the copper tube, *A*, containing the compressed oxygen, and was there evaporated at a temperature of about −140°, thus cooling

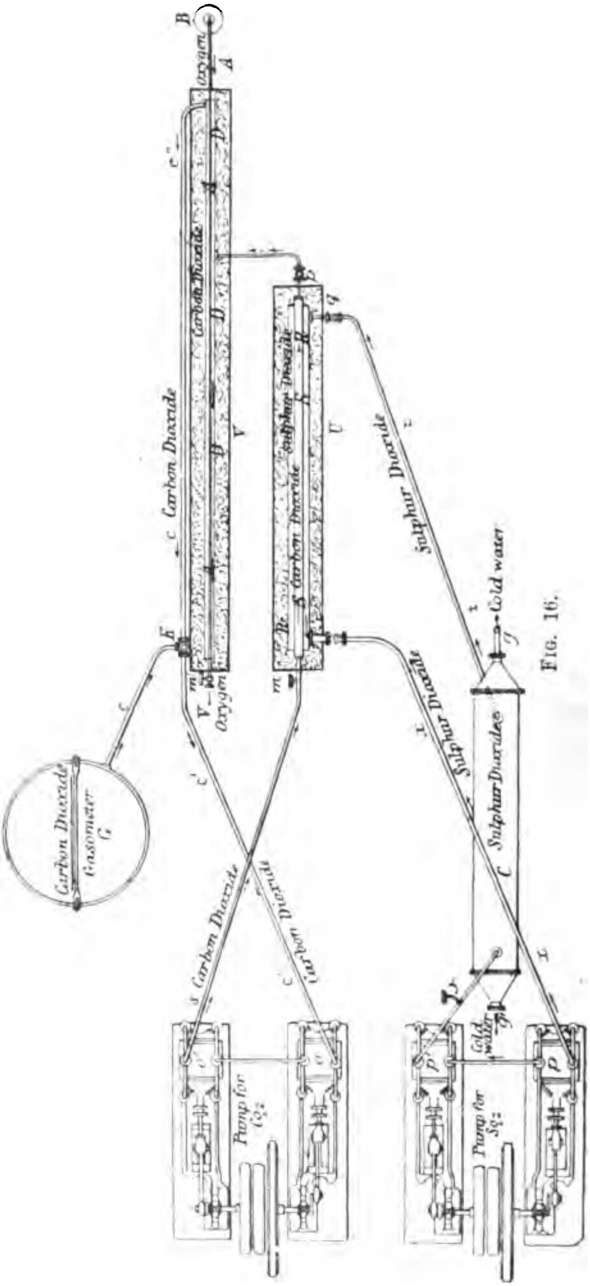
B
A
Oxygen
c''
D
Carbon Dioxide
c Carbon Dioxide
V
D
U
q
Sulphur Dioxide
Carbon Dioxide
E
m
V
Oxygen
Carbon Dioxide
Gasometer G
c
c'
s Carbon Dioxide
c' Carbon Dioxide
Pump for CO_2
x
Sulphur Dioxide
C Sulphur Dioxide
Cold water
g
Cold water
P'
P
Pump for SO_2

FIG. 16.

the oxygen well below its critical temperature (−119°). With this apparatus oxygen was first liquefied on the 22nd December, 1877, at a temperature of −140° and a pressure of 320 atmospheres. In the course of another experiment the oxygen attained a pressure of about 500 atmospheres and remained constant at 475 atmospheres. On opening the stopcock at the end of the oxygen tube, a lustrous jet of liquid oxygen issued with great violence, whilst around it was a haze of particles of what was taken to be solid oxygen. It will be observed that these pressures are greatly in excess of the critical pressure of oxygen (p. 101).

CAILLETET'S PROCESS FOR LIQUEFYING GASES.

55 The apparatus employed by M. Cailletet[1] for the liquefaction of oxygen is shown in Fig. 17, and consists of a powerful hydraulic press by means of which the gas contained in the receiver (a m, Fig. 17; Fig. 18) can be strongly compressed and then allowed to expand rapidly.

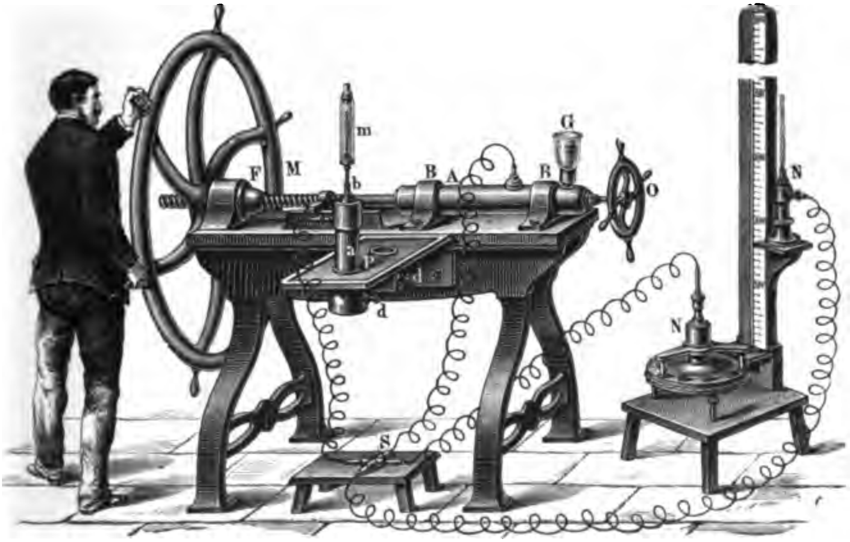

FIG. 17.

The receiver consists of a glass tube with reservoir at the lower end which is firmly bedded into a steel head (B, Fig. 18)

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[1] *Compt. Rend.* 1877, **85**, 815; *Ann. Chim. Phy.* 1878, [5], **15**, 132.

sufficiently strong to resist the pressure of 1,000 atmospheres, and is placed in direct connection with the hydraulic pump by means of a flexible metallic tube (T U) of small diameter. A steel head is firmly screwed on to the upper part of the receiver by the screw (E′), and this head carries the glass tube (T), which contains the gas to be experimented upon, the lower portion of this tube dipping into the mercury which fills the lower part of the steel receiver. As the glass reservoir is exposed to the same pressure on both its inside and outside surfaces, its dimensions may be made large in spite of the extremely high pressures to which it is subjected in the course of the experiments. The thin tube, on the other hand, which passes out above the steel head of the condenser has, of course, to support the pressure necessary for the condensation of the gases, and hence it must be made of strong glass with a capillary bore. A glass cylinder (M) resting on the iron flange (S) serves to enable the experimenter to surround the tube either with a freezing-mixture or with a warm liquid. When the reservoir has been filled with

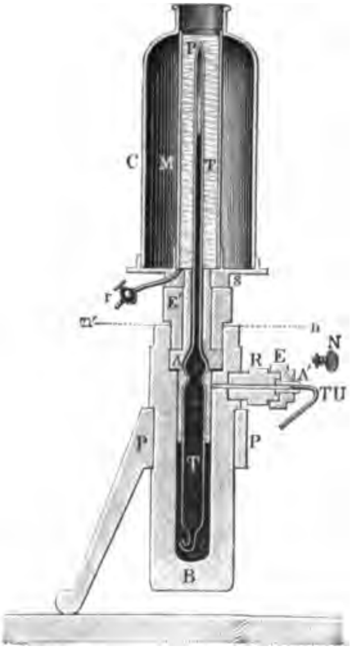

FIG. 18.

the pure dry gas under examination the end of the tube is carefully hermetically sealed, and the whole screwed into position. Water is then forced into the receiver from the hydraulic cylinder; this forces the mercury into the reservoir, and the compressed gas condenses in the capillary tube, where the changes which occur can be readily observed.

With this apparatus Cailletet liquefied ethylene at + 4° under a pressure of 46 atmospheres; acetylene under the ordinary temperature at a pressure of 86 atmospheres; nitric oxide and marsh gas required to be cooled to $-11°$, and these became liquid at the respective pressures of 104 and 108 atmospheres. Oxygen and carbon monoxide remained gaseous at a temperature of $-29°$ under a pressure of 300 atmospheres, as did nitrogen at a temperature of + 13° and under a pressure of 200 atmospheres. When, however, this pressure was suddenly reduced, a thick mist was formed in the tubes, and this condensed, forming small drops. Hydrogen, on the other hand, appeared, when the pressure from 300 atmospheres was suddenly removed, in the form of a slight mist, but dried air liquefied under a pressure of 200 atmospheres after it had been well cooled with liquid nitrous oxide.

56 The principles employed by Pictet and Cailletet were modified and used in conjunction by many subsequent workers, the gases being only moderately compressed, cooled by liquid ethylene boiling under diminished pressure, and then allowed to expand. In this way the liquefaction was effected of all the so-called permanent gases in quantity, with the single exception of hydrogen, which was only obtained in the form of a mist (Wroblewski).

The physical constants of the liquid gases, including hydrogen, were determined with great care by Wroblewski and Olszewski, whilst Dewar, in possession of much larger quantities, devoted himself to the study of chemical action and the properties of matter at low temperatures.

The manipulation of liquid gases, such as air and oxygen, at the atmospheric pressure has been rendered easy by Dewar's invention of the vacuum vessel. This consists of a double-walled glass vessel, the space between the walls of which is evacuated, Fig. 19. The absence of air from this space does away with the conveyance of heat to the liquid by convection, so that the sole sources of heat are radiation and conduction along the glass, both of which are small compared with the convection, whilst the radiation can be still further diminished by silvering the glass. In these vessels liquid air may be preserved for many hours, and it can readily be poured into other vessels, syphoned off, filtered through paper, and, in fact, manipulated like any other volatile liquid.

57 A new principle was introduced in 1895, almost simultaneously by Hampson and Linde, which has greatly simplified the production of liquid air, and, in the hands of Dewar, has led to the production of liquid hydrogen in quantity. The novelty of the method consists in allowing the strongly compressed gas to expand at a valve placed at the lower end of a copper coil wound spirally about a vertical axis. The escaping gas, cooled by expansion, passes over the surface of the coil, and thus cools the compressed gas within it, which, in its turn, expands, and is thus still further cooled. This "self-intensive" cooling goes on until finally a temperature is reached at which the escaping gas (air, oxygen, or nitrogen) becomes liquid, the entire cooling being brought about by the expansion of the gas itself. In this process the main cooling effect appears to be due, not to the performance of external work, but to the performance of internal work, which probably consists in overcoming the mutual attraction of the molecules of the highly compressed gas. This phenomenon—the cooling which occurs when a highly compressed gas is allowed to expand in such a way that no external work is done—is known as the Joule-

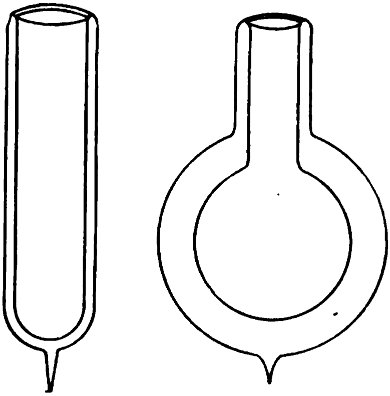

FIG. 19.

Thomson effect,[1] and amounts in the case of air to 0·2 – 0·25° C. per atmosphere of pressure.

The installation required for the production of liquid air by this means at the rate of about 1 litre per hour[2] is shown in diagrammatic section in Fig. 20.

Air is drawn over trays containing lime, *A*, and is compressed by a pump to 160–180 atmospheres in the cylinders *B* and *D*, which are cooled by water, and then passes through a water separator, *F*, and a cylinder, *H*, containing solid caustic potash, to remove moisture and carbon dioxide, to the self-intensive coil, *K*, where it is allowed to expand at the valve, *L*, regulated by means of the screw-head and rod, *M*. The expanded gas escapes over the surface of the coil, and, leaving at *P*, passes back to *A*. The coil is carefully insulated to prevent access of heat, and the lower portion, or even the whole of it, is placed within a Dewar vacuum vessel, *N*, in which the liquid collects. About 5 per cent. of the air which passes through the pump is obtained in the liquid form. Some workers prefer to give the gas a preliminary cooling by means of liquid carbon dioxide before passing it through the coil, the latent heat of carbon dioxide being thus utilised for this portion of the cooling instead of the Joule-Thomson effect.

58 *Liquefaction of Hydrogen.*—Hydrogen was found by Joule and Thomson to become hotter instead of cooler when expanded in such a way that the Joule-Thomson effect could be measured, and, moreover, it does not appear to become progressively cooler when expanded in the Hampson apparatus from a pressure of 200 atmospheres at – 80°. When, however, the hydrogen compressed at 200 atmospheres is cooled by liquid air boiling under diminished pressure to a temperature below – 200°, and is then allowed to expand, cooling occurs, and the gas finally becomes liquid. The liquefaction of hydrogen was first effected by Dewar in this way on May 10th, 1898, by means of an apparatus which has not been fully described. Liquid hydrogen can now readily be prepared by making use of a modified form of Hampson's apparatus,[3] in which the compressed gas is cooled successively by solid carbon dioxide and ether, liquid air boiling at the atmospheric

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[1] Compare Clerk-Maxwell, *Theory of Heat*, Chap. 13.
[2] Travers, *Experimental Study of Gases*, p. 190.
[3] Travers, *Phil. Mag.* 1901, [6], 1, 411.

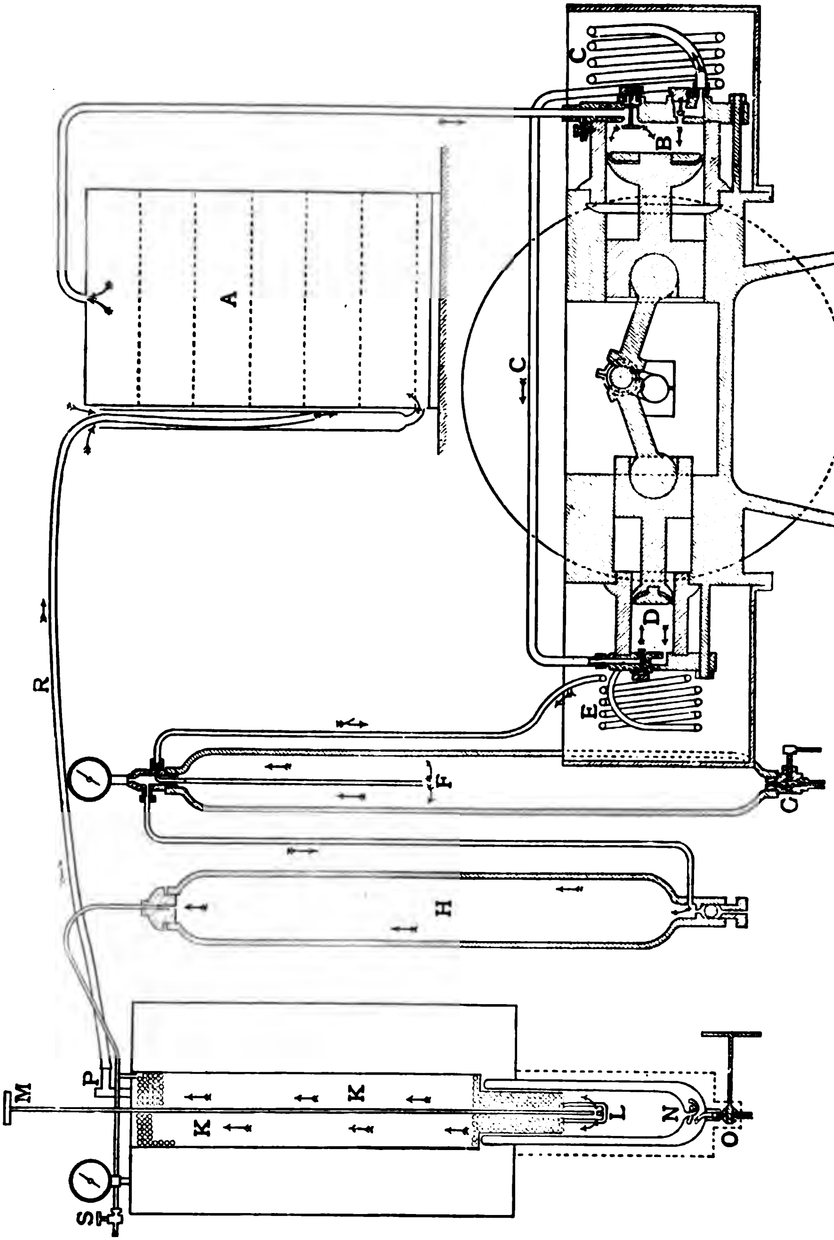

FIG. 20.

pressure, and liquid air boiling under diminished pressure. It then passes through a coil enclosed in a vacuum vessel, and expands at an annular valve.

Liquid hydrogen boils at −252-253°, and when it is allowed to boil under diminished pressure freezes to an ice-like solid, melting at −256–257°; the lowest temperature hitherto reached has been attained by the rapid evaporation of the liquid, and is −260°, or 13° on the absolute scale (Dewar).

Helium is, at the moment, the only gas which has not yet been liquefied. The question whether the liquefaction can be effected by cooling the compressed gas with liquid hydrogen boiling in vacuo, and then expanding it in a self-intensive manner, has not yet been decided.

LIQUIDS.

59 It is evident from what has been said that the distinction between gas and vapour is only one of degree, for a vapour is simply a gas below its critical temperature. The same laws according to which the volumes of gases vary under change of temperature and pressure apply also to vapours, at any rate when they are examined at temperatures considerably above their points of condensation. When a vapour is near its point of condensation its density increases more quickly than the pressure, and as soon as the point is reached the least increase of the pressure brings about a condensation of the whole to a liquid.

The essential difference between a liquid and the vapour from which it is produced lies in the fact that the liquid possesses a definite surface tension, and consequently occupies a definite volume limited by a surface, and is not capable, like a gas, of filling any space into which it may be brought. At the surface of the liquid evaporation occurs at all temperatures, and this continues until the pressure of the vapour reaches a certain definite value which depends on the temperature. This value is known as the vapour pressure (or less happily as the vapour tension) of the liquid at that particular temperature, and is always reached when an excess of the liquid is present. *When the vapour pressure is equal to the superincumbent pressure the liquid is said to boil*, the corresponding temperature being termed the boiling point of the liquid. The boiling points usually quoted refer to the normal atmospheric pressure of

760 mm. of mercury, and a list of those of some well-known substances is given on p. 101.

60 Liquids possess a notable vapour pressure below their boiling-points; thus water gives off vapour at all temperatures, and even slowly evaporates when in the solid state, for the pressure of the vapour coming from ice at −10° is 0·208 mm. According to the experiments of Faraday, there is, however, a limit beyond which evaporation cannot be detected; thus he found that mercury gives out a perceptible amount of vapour during the summer, but that none could be detected during the winter, and that certain compounds which can be volatilised at 150° undergo no perceptible evaporation when kept for years at the ordinary temperature. Dalton[1] in 1801 discovered that this maximum pressure or density of a vapour is not altered by the presence of other gases, or, in other words, that the quantity of a liquid which will evaporate into a given space is the same whether the space is a vacuum or is filled with another gas. The same philosopher also believed that the vapours of all liquids possessed an equal pressure at temperatures equally distant from their boiling-points. Regnault[2] has, however, shown by exact experiments that the above conclusions can only be considered as approximately true, inasmuch as he found that about 2 per cent. *more* vapour ascends into a space filled with gas than into a vacuum, whilst at considerable but equal distances from the boiling-point the pressures of volatile liquids are by no means equal.

It has now been found that in comparing different liquids the essential factors to be considered are the critical constants, and, when these are adopted as the basis of comparison, numerous important relations become apparent.[3] Thus at *corresponding temperatures*—*i.e.* temperatures which are the same fractions of the critical temperatures of the liquids in question, as measured on the absolute scale—different liquids have vapour pressures which are also the same fraction of the critical pressures of the liquids.

These relations, however, only hold strictly for substances of similar chemical constitution. Thus, fluobenzene, C_6H_5F, boils

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[1] *Manch. Memoirs*, 1st series, **5**, 535.

[2] *Mémoires de l'Acad. des Sciences*, **21**, 465.

[3] Van der Waals, *Continuität des flüssigen und gasförmigen Zustandes.* Ramsay and Young, *Zeit. physikal. Chem.* 1887, **1**, 237, 433. Young, *Phil. Mag.* 1892 [5], **33**, 153.

at 358·1° Absolute (85·1° C.) and has the critical temperature 559·55° Absol. and the critical pressure 33,912 mm. Let us compare this with chlorobenzene, C_6H_5Cl, which has a critical temperature of 633° Absol. and the same critical pressure as fluobenzene.

Fluobenzene at its boiling point, 358·1° Absol., which is 358·1/559·55 = 0·639 of the critical temperature, has the pressure of 760 mm. = 0·00224 × 33912 (the critical pressure). According to the law of corresponding states, chlorobenzene at the *corresponding* temperature should have a *corresponding* pressure. Now the corresponding temperature is 0·639 × 633 = 404·5° Absol., and the pressure at this temperature should therefore be 0·00224 × 33912 = 760 mm., 33912 being the critical pressure and 633° the critical temperature of chlorobenzene.

This agrees well with experiment, according to which the pressure at 404·5° Absol. is 763·8 mm.

The values of these critical constants themselves can be calculated by means of Van der Waals' equation (p. 97) from the properties of the gases, and it is a remarkable illustration of the continuity of the gaseous and liquid states that this equation, which was devised to express the relations between pressure, volume, and temperature for gases, can be applied directly to the liquids produced by the condensation of these gases.

THE MOLECULAR WEIGHTS OF LIQUIDS.

61 The molecular weights of substances in the liquid state can be determined with some degree of certainty by measuring the rate of change of their molecular surface energy with change of temperature. The details of the practical execution of the determination, which involves the measurement of the capillary rise of the liquid at different temperatures, and the discussion of the theoretical basis upon which it is founded, must be sought in the original paper.[1]

From such experiments it appears that in many cases the molecules which make up the liquid have precisely the same weight as those of the substance in the gaseous state. This is true for such substances as carbon bisulphide, CS_2, phosphorus trichloride, PCl_3, silicon tetrachloride, $SiCl_4$, thionyl chloride, $SOCl_2$, benzene, C_6H_6, and many others. In other liquids, such

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[1] Ramsay and Shields, *Journ. Chem. Soc.* 1893, 1082.

as the organic acids and alcohols, the molecules are two, three, or four times as heavy as those of the corresponding gases. This is also the case with water, the molecular weight of which at ordinary temperatures approaches that corresponding with the formula $(H_2O)_4$.

THE PROPERTIES OF SOLUTIONS.

62 Concerning the relation between the dissolved substance and the solvent in a concentrated solution, but little is known. Many such solutions, when cooled, deposit crystals which contain a portion of the solvent combined with the substance which has been dissolved. It has, therefore, been supposed that the solutions in these cases actually contain these compounds. On the other hand, it has been held that no compounds are present in the solutions, but that the combination takes place at the moment of separation of the solid substance, and this view is rendered more probable by the fact that in many cases different hydrates can be obtained by appropriate means from the same solution.

63 Until recently the molecular condition of substances in dilute solution was quite unknown, but much light has been thrown upon the subject by the researches of Raoult, Van't Hoff, Arrhenius, Ostwald, and others,[1] who have shown that a remarkable analogy exists between the properties of substances in dilute solution and those of gases. This conclusion has been chiefly derived from the study of the interesting phenomena now to be described. When a solution of a crystalloid substance in water is placed in a vessel closed by a porous membrane, such as a piece of parchment, and the whole immersed in pure water, it is found that the dissolved substance gradually passes outwards through the film of parchment, whilst water passes inwards, until, after a sufficient time has elapsed, equilibrium is established and the liquid has the same composition both inside and outside the membrane, this process being known as *osmosis*.

Diaphragms of other substances can, however, be obtained which allow the water to pass freely through them in the same way as the parchment, but prevent the outward passage of the

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[1] For a full account of this subject the text-books of Ostwald, Nernst, Walker, and others may be consulted.

dissolved substance, and are therefore said to be "semi-permeable." Such a diaphragm can be prepared by filling an ordinary porous cell with a dilute solution of potassium ferrocyanide and simultaneously immersing it in one of copper sulphate. These two substances gradually diffuse into the porous walls of the cell and produce an insoluble layer of copper ferrocyanide, which is found to be semi-permeable for solutions of many salts and other bodies. If now such a cell, containing a dilute solution of sugar, be placed in a vessel containing pure water, the latter is found to pass inwards through the film, whilst the sugar does not pass out, and consequently the level of the liquid within the cell rises. If, however, the cell be completely filled and connected with an arrangement for measuring the pressure it will be found that the latter gradually increases, but after a time becomes constant. The pressure thus observed is termed the *osmotic pressure* of the solution, and is found to depend only upon (1) the nature of the dissolved substance, (2) the concentration of the solution, and (3) the temperature.

This osmotic pressure plays the same part in the theory of dilute solutions as the gaseous pressure in that of gases, and is found to follow the same laws. Thus when the strength of the solution is doubled the osmotic pressure becomes twice as great; when it is halved the pressure falls to one-half, and so on. Now doubling the strength of a solution is in reality halving the volume occupied by the unit weight of the dissolved substance, so that the law that the osmotic pressure of a dilute solution varies directly as its concentration corresponds exactly with Boyle's law of gases (p. 83). This is well seen in the following table, which illustrates the variation of osmotic pressure with the concentration for solutions of cane sugar:[1]

Strength of sugar solution.	Osmotic pressure.	Pressure per gram of sugar.
1 g. per 100 c.c.	53·5 cm.	53·5 cm.
2 "	101·6	50·8
4 "	208·2	52·1
6 "	307·5	51·2

The osmotic pressure is also found to vary with the temperature in the same way as does the pressure of gases. Thus a solution of cane sugar was observed to have an osmotic

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[1] See Pfeffer, "Osmotische Untersuchungen," 71, quoted in *Zeit. physikal. Chem.* 1887, **1**, 484.

pressure of 54·4 cm. at 32°, whilst the same solution at 14·1° had a pressure of 51·2 cm. Calculating the pressure at the lower temperature from that at the higher according to Dalton's law for gases (p. 84) we obtain the number $\frac{54{\cdot}4 \times 287{\cdot}1}{305} = 51{\cdot}0$, or almost exactly that observed.

64 Another remarkable fact which these researches have established is that solutions of substances which contain quantities of the dissolved compounds proportional to their molecular weights in equal volumes of the solution possess the same osmotic pressure; if we consider cane sugar (molecular weight 340) and alcohol (molecular weight 46), for example, we find that a solution of sugar in water containing 3·40 grams in 100 c.c. has the same osmotic pressure as one of 0·46 grams of alcohol in the same volume. Moreover it appears that the osmotic pressure of a solution is numerically equal to the pressure of a gas containing the same number of molecules per unit of volume as the solution does of molecules of the dissolved substance. A solution of 1 gram of sugar in 100 c.c. of water, for example, has at 15° the specific gravity of 1·004, so that 1 gram of sugar is contained in 100·6 c.c. of the solution. Now the molecular weight of sugar is 340, and if we calculate what volume of this solution contains 340 grams of sugar, we obtain the number 34·2 litres. We know that two grams of hydrogen (the molecular weight of which is 2) at a temperature of 15° occupy a volume of $\frac{22{\cdot}25 \times 288}{273} = 23{\cdot}53$ litres when the pressure is equal to one atmosphere. If this volume of the gas be expanded to 34·2 litres the pressure of the expanded gas will, by Boyle's law, be equal to $\frac{760 \times 23{\cdot}53}{34{\cdot}2}$, that is to say 52·3 cm. The gas therefore which contains the same number of molecules per litre as there are sugar molecules per litre in such a solution of cane sugar, would, at the temperature of 15°, have a pressure of 52·3 cm., whilst the osmotic pressure of the solution itself has been found to be 52·9 cm.

As a consequence of these remarkable relations it will be seen that the molecular weight of a dissolved substance can be determined by measuring the osmotic pressure of the solution, but the experimental difficulties are so great as to prevent the general use of the method for this purpose.

65 The same result can, however, be attained by several

allied methods, the chief of which depends upon the alteration produced in the freezing-point of a liquid by dissolving some other substance in it. When a dilute solution, such as one of sugar in water, is cooled, the solvent, in this case the water, begins to separate out, and, if the solution be originally sufficiently dilute, the solid matter which deposits is quite free from the dissolved substance. The temperature at which the separation of solid matter commences is, however, lower than the freezing-point of the pure solvent, the amount of the depression being proportional to the concentration of the solution (Blagden).[1]

Raoult has further found that the extent of the depression depends upon the molecular weight of the dissolved substance, to which it is inversely proportional, or, in other words, that if equal weights of a series of compounds be each dissolved in a liquid so as to produce equal volumes of solution, the depressions of the freezing-point thus caused are inversely proportional to the molecular weights of the compounds. If these depressions be then multiplied by the molecular weights of the compounds a constant number is obtained, which is known as the *molecular depression* for the solvent in question. This is illustrated by the following table of results obtained by Raoult[2] with substances dissolved in acetic acid:

Substance.	Formula.	Molecular Weight.	D.	MD.
Carbon tetrachloride	CCl_4	153	0·252	38·6
Carbon bisulphide	CS_2	76	0·505	38·4
Sulphur chloride	S_2Cl_2	134	0·286	38·3
Arsenious chloride	$AsCl_3$	180	0·234	42·1
Stannic chloride	$SnCl_4$	258	0·159	41·0
Sulphur dioxide	SO_2	64	0·601	38·5
Sulphuretted hydrogen	H_2S	34	1·047	35·6

In this table D signifies the depression in degrees Centigrade produced by 1 grm. of substance dissolved in 100 grms. of glacial acetic acid,[3] whilst MD is the product of this number with the molecular weight of the compound. It will be seen that the molecular depression for this solvent is nearly constant, the numbers varying on either side of an average value of about 39.

66 The addition of a soluble substance to a liquid not only

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[1] *Phil. Trans.* 1788, **78**, 277.

[2] *Ann. Chim. Phys.* 1884 [6], **2**, 93.

[3] The slight differences between the resulting volumes of solution are here neglected.

lowers the freezing-point of the latter, but also diminishes its vapour-pressure and raises its boiling-point. Like the depression of the freezing-point, this diminution of vapour-pressure or rise in boiling-point depends upon the molecular weight of the dissolved substance and upon the strength of the solution.

These three classes of phenomena—osmotic pressure, depression of the freezing-point, and diminution of vapour-pressure—are intimately connected with one another, inasmuch as it has been experimentally found that dilute solutions, the solvent being the same in all, which have the same osmotic pressure have also the same freezing-point and the same vapour-pressure, such solutions being termed *isotonic*. This relation has also been deduced theoretically, so that if any one of these three facts be known about a solution the other two can be calculated.

It is important to remember that these statements only hold good in the case of *dilute solutions*, and cannot be applied to concentrated solutions, just as the laws of Boyle and Dalton do not apply without modifications to gases at high pressures and low temperatures.

AQUEOUS SOLUTIONS.

67 The behaviour of aqueous solutions when examined by the methods just described is somewhat anomalous, but an explanation of the irregularities observed has been arrived at from a study of the phenomena which occur when an electric current is passed through such solutions. Pure water is almost a non-conductor of electricity, and substances which are soluble in it may be divided into two classes, according as they do or do not produce solutions which conduct electricity. Those of the former class are termed *electrolytes*, and the passage of the current through their solutions is accompanied by their decomposition, whilst those of the second class are known as *non-electrolytes*. The laws of osmotic pressure, &c., as stated above are true of all non-electrolytes, but require some modification before they can be applied to electrolytes, a class of bodies which includes acids, alkalis, and almost all metallic salts. When the molecular weight of one of these substances is determined from an aqueous solution by any of the methods described, the number obtained is found to be some fraction of that which was to be expected, generally about $\frac{1}{2}$ or $\frac{1}{3}$.

This result is comparable with that obtained by the vapour-density method with such vapours as undergo dissociation, and it seems probable that something of an analogous nature also occurs in dilute aqueous solutions of electrolytes. When a current of electricity is passed through a solution of hydrochloric acid, HCl, hydrogen is given off at the negative pole and chlorine at the positive, and the acid is said to have been decomposed into the two "ions" hydrogen and chlorine. Many facts make it appear probable that this decomposition is not actually brought about by the electric current but that the ions exist already separated in the solution. According to this view, then, a dilute solution of hydrochloric acid does not only contain molecules of HCl but a large proportion of separated electrically-charged ions H and Cl. Each one of these ions behaves like a molecule of a non-electrolyte and, therefore, produces its own effect in lowering the freezing-point, &c., the total depression being due to the sum of the ions, each considered as an independent molecule, together with the unaltered molecules. Since the depression is inversely proportional to the molecular weight, the result obtained by this method seems to show that hydrochloric acid has about one-half of the molecular weight corresponding to the formula HCl. In general, salts, such as common salt, NaCl, or silver nitrate, $AgNO_3$, which are broken up into two ions (Na and Cl, Ag and NO_3), appear to have about half the calculated molecular weight, whilst the salts of a dibasic acid or a divalent metal of the types represented by sodium sulphate, Na_2SO_4, and calcium chloride, $CaCl_2$, which give three ions (Na, Na and SO_4; Ca, Cl and Cl), appear to have a molecular weight approaching one-third of that calculated.

According to this theory of "electrolytic dissociation" which is due to the Swedish physicist Arrhenius, the greater number of salt molecules in a strong solution of an electrolyte are unaltered, but some of them have been dissociated into their ions; when the solution is diluted the number of dissociated molecules increases rapidly, and in a very dilute solution nearly all the salt is present in the form of ions. The following table shows the percentage of dissociation which would account for the results obtained by the freezing-point method for a few common salts:[1]

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[1] Arrhenius, *Zeit. physikal. Chem.* 1887, **2**, 491.

	Grms. in 100 c.c. water.	Percentage of molecules dissociated.	
NaCl	0·682	87	into 2 ions.
„	3·155	79	
$AgNO_3$	2·381	85	
$CaCl_2$	2·206	75	into 3 ions.
K_2SO_4	1·583	67	

Another method which may be employed for the same purpose is the measurement of the electrical conductivity of the solution. It is found that when a moderately strong solution of a salt is diluted, the conductivity per unit of dissolved substance increases, and, as the dilution proceeds, approaches a definite limit, which may be taken as the conductivity of the salt when dissolved in an infinite amount of water so as to make a solution of infinite dilution. This is shown in the following table for solutions of potassium chloride. The numbers in the second column represent the relative conductivity for a fixed amount of salt in solutions which contain *m* gram-molecules of the salt per litre, the values of *m* being given in the first column:—

m.	Conductivity.	Percentage of dissociated molecules.
2	864	71
1	911	75
0·1	1,047	86
0·01	1,147	94
0·001	1,193	98
0·0001	1,209	99
Limit.	1,220	100

The percentage of dissociation in any given solution is then represented by the ratio of the actual conductivity of the substance in that solution to its conductivity in a solution of infinite dilution. The numbers in the third column of the table above show the amount of dissociation into two ions which occurs in the case of potassium chloride in the various solutions. The results obtained by this method agree generally with those obtained by the freezing-point method.

Each ion is supposed to bear a charge of electricity, electropositive ions having a positive, electronegative a negative charge, whilst the charge on a triad ion (p. 140) is three times, and on a dyad ion twice that carried by a monad ion. When, therefore, it is said that a dilute solution of hydrochloric acid contains free ions of hydrogen and chlorine, it must not be supposed that what we are familiar with as free hydrogen and chlorine are meant; what are actually present are positively-charged atoms (ions) of hydrogen and negatively-charged atoms (ions) of chlorine. These charged ions cannot escape from the solution without giving up their charges of electricity to some oppositely-charged body, and this is what happens at the poles of the electrolytic cell during electrolysis. The hydrogen ions give up their positive charges to the negatively-charged pole and escape as free hydrogen, the atoms uniting to form molecules, whilst the chlorine ions behave in a similar manner at the positively-charged pole. In many cases the liberated atoms enter into reaction with the water surrounding the pole and thus give rise to secondary products which either escape or remain in the solution.

Concerning the exact nature of the separation of the ions our knowledge is still incomplete, but many facts in addition to those already adduced point to the conclusion that such a separation does actually take place.

68 One of the most important arguments in favour of this view is afforded by the circumstance that almost all the properties of such dilute solutions have been shown to be equal to the sum of the properties of the ions. Each ion has a definite weight, volume, colour, &c., and the effect produced by a salt is found to be equal to the sum of the effects which would be independently produced by the ions into which it is capable of being decomposed. This has already been explained for the osmotic pressure, freezing-point and vapour-pressure of solutions, and also holds for the colour, specific gravity, refractive index, &c.

This theory is, therefore, in accordance with the physical properties of such solutions, and it moreover throws great light upon many chemical reactions. Chemical action occurring in dilute solution, according to this view, takes place between the ions of the substances concerned, so that the tests usually applied for the metals and acids are in reality tests for the corresponding ions. Thus, for example, the tests for ferrous salts fail to detect iron in potassium ferrocyanide, $K_4FeC_6N_6$, although they are given by ferrous sulphate, $FeSO_4$. This is due to the fact that in the latter case the ion of ferrous iron is present in the solution, whilst in the former the ions are K and the complex group FeC_6N_6.

The fact that the same amount of heat is evolved by the neutralisation of any of the strong acids by any of the strong bases also receives a new and interesting interpretation in the light of this theory. Taking the case of the action of hydrochloric acid on caustic soda, which is usually represented by the equation,

$$\mathrm{NaHO + HCl = NaCl + H_2O},$$

we see that the action takes place between the ions in the following way:

$$\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{HO}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} = \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} + \mathrm{H_2O}.$$

The result of the reaction is simply the formation of water, since the Na and Cl ions remain dissociated. Exactly the same reaction takes place if another acid and a different base be employed:

$$\overset{+}{\mathrm{K}} + \overset{-}{\mathrm{HO}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{NO_3}} = \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{NO_3}} + \mathrm{H_2O}.$$

The amount of heat evolved is, therefore, also the same.

The application of this theory to the properties of acids and bases in dilute solution will be found in Vol. II. (1897), pp. 85–89.

EXPERIMENTAL METHODS FOR THE DETERMINATION OF MOLECULAR WEIGHTS.

69 We have seen above (p. 75) that the molecular weight of every compound in the gaseous state is twice its density with respect to hydrogen, from which it follows that in order to determine the molecular weight of a substance it is simply necessary to determine its density in the state of gas. This process can be readily applied to such substances as are gases under ordinary conditions of temperature and pressure, and also to such as can be rendered gaseous by moderate increase of temperature, but is of course inapplicable to bodies which decompose on heating or which cannot easily be vaporised. In such cases, however, several methods are available which depend upon the properties of solutions, and hence, since

nearly all chemical compounds are soluble in some liquid, the molecular weight of a body can almost always be determined.

Special experimental methods have to be adopted for each of these classes of substances.

I. DETERMINATION OF THE MOLECULAR WEIGHTS OF PERMANENT GASES.

70 For this purpose it is only necessary to determine the specific gravity of the gas, air being usually taken as the practical unit of comparison. A large glass balloon, capable of holding from 1 to 10 litres of the gas, is employed and is first of all freed from air as far as possible by the vacuum pump, and weighed. In weighing a body of such large volume it is essential to make allowance for the buoyancy of the air, since the body to be weighed appears to be lighter than it really is by an amount equal to the weight of the air which it displaces. This is best accomplished by suspending a vessel of similar size and shape to the other arm of the balance, by which arrangement the effect of buoyancy is neutralised, each of the vessels being affected in the same manner, and at the same time the uncertainties of calculation due to the varying temperature, pressure, and moisture of the atmosphere are avoided, as well as any inaccuracy due to condensation on the surface of the glass. As soon as the weight of the empty vessel has been ascertained, it is removed from the balance and filled with the pure dry gas, the temperature and pressure being carefully observed. The globe is then reweighed with the same precautions as before. One additional correction must be here noticed, as it gives rise to a considerable error especially when light gases are being weighed. The capacity of a vacuous globe of glass is found to be perceptibly less than that of the same globe when filled with gas at the pressure of the atmosphere, and hence the globe displaces less air in the former condition than in the latter. The difference between the corrected weights of the globe empty and filled with the gas is equal to the weight (W) of the given volume of gas at the observed temperature and pressure. The same globe is then filled with dry air freed from carbonic acid gas, or else with pure hydrogen, and the weight of an equal volume of the latter (A) under the same conditions thus ascertained. The specific gravity of the gas compared with air is then equal

to $\frac{W}{A}$. Since air has been found to be 14·39 times as heavy as hydrogen and the molecular weight of a gas is twice its density with respect to hydrogen, it is only necessary to multiply the specific gravity by $14·39 \times 2$ to obtain the molecular weight of the gas in question.

The most accurate determinations of this kind have been made by Regnault, and more recently by Rayleigh, Leduc, Morley, &c.

II. DETERMINATION OF THE MOLECULAR WEIGHTS OF VOLATILE LIQUIDS AND SOLIDS.

71 A detailed account of the various methods proposed for this purpose is to be found in a later volume (Vol. III. Pt. I. pp. 84–112); only the two most frequently employed will be here briefly described.

The specific gravity of the vapour of a liquid or solid can be determined in two ways; either by weighing the vapour which occupies a known volume under given conditions of temperature and pressure (Dumas' method) or by measuring the volume occupied under given conditions by the vapour of a known weight of the liquid or solid (Gay-Lussac, Hofmann, Victor Meyer).

I. METHOD OF DUMAS.

72 For this purpose a thin glass globe is employed of 150–200 cubic centimetres in capacity, having a finely drawn-out neck (Fig. 21); the exact weight of the globe, weighed in air and filled with dry air at a certain temperature and pressure, having been found, a small portion of the substance of which the vapour-density is to be determined is brought inside, and the globe then heated by being plunged into a water- or oil-bath raised to a temperature at least 30° above the boiling-point of the substance (Fig. 22); as soon as the vapour has ceased to issue from the end of the neck, this end is hermetically sealed before a blow-pipe, and the exact temperature of the bath as well as the barometric pressure observed. The bulb thus filled with vapour is carefully cleaned, allowed to cool, and accurately weighed. The point of the neck is next broken under water,

which rushes into the globe, the vapour having condensed, and, if the experiment has been well conducted, completely fills it. The bulb is then weighed full of water, and its capacity calculated from the weight of water which has entered.

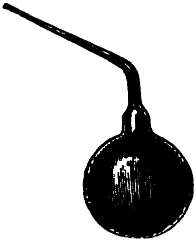

FIG. 21.

We have now all the data necessary for the determination. In the first place we have to find the weight of the given volume of the vapour under certain conditions of temperature and pressure, and we then have to compare this with the weight of an equal volume of hydrogen gas measured in the same circumstances. The following example of the determination of the vapour density of water may serve to illustrate the method:—

FIG. 22.

Weight of globe filled with dry air at 15·5°	23·449 grams.
Weight of globe filled with vapour at 140°	23·326 „
Capacity of the globe	178 c.c.

As the barometric column (760 mm.) underwent no change from the beginning to the end of the experiment, no correction for pressure is necessary. In order to get at the weight of the vacuous globe the weight of air contained must be deducted from the weight of the globe in air.

Now 1 c.c. of air at 0° and 760 mm. weighs 0·001293 gram. and 178 c.c. of air at 15·5° would occupy $\frac{178 \times 273}{288 \cdot 5} =$ 168·4 c.c. at 0°, so that the weight of this air is $168 \cdot 4 \times 0 \cdot 001293 = 0 \cdot 218$ gram; hence the weight of the vacuous globe is 23·231 ($23 \cdot 449 - 0 \cdot 218$), and the weight of the vapour $23 \cdot 326 - 23 \cdot 231 = 0 \cdot 095$ gram. We must now find what 178 c.c. of hydrogen at 140° will weigh. One thousand c.c. of hydrogen at 0° weigh 0·0899 gram; 178 c.c. at 140° will contract to $\frac{178 \times 273}{413} = 117 \cdot 6$ at 0°, which weigh $\frac{117 \cdot 6 \times 0 \cdot 0899}{1000} = 0 \cdot 0106$ gram. Hence $\frac{0 \cdot 095}{0 \cdot 0106} = 8 \cdot 96$ is the density of the vapour as found by experiment.

The molecular weight of water is therefore about 17·92. In this example many minor corrections, such as the expansion of the glass globe, the error of the mercurial thermometer, &c., are not considered, but the above method carried out as described gives results which are sufficiently accurate when the object, as in this case, is to control the molecular weight of a compound.

II. METHOD OF VICTOR MEYER.

73 The glass vessel (*b*, Fig. 23) filled with air is heated by the vapour of water or other liquid placed in the bulb tube (*c*), which may if necessary be replaced by an air-bath, until no more air is observed to pass out of the gas delivery tube (*a*). The cork (*d*) is then removed and the weighed quantity of the substance of which the vapour-density is required, contained in a small glass bulb, is dropped into the tube (*b*) and the cork then quickly inserted; the substance rapidly evaporates and displaces a portion of the air of the apparatus which is collected in a

graduated tube over water and carefully measured. This method has the great advantage of dispensing with a knowledge of the temperature to which the tube is heated. It is to be borne in mind that what we require to know is the weight of air (or hydrogen) equal in bulk to the vapour. Whether this volume of air be measured at the temperature of the vapour or at that of the atmosphere, it has of course the same weight.

An example will make this clear. In a determination of the molecular weight of chloroform, $CHCl_3$, heated by water vapour, it was found that 0·1008 gram of substance displaced 20 c.c. of air, measured over water at a temperature of 15° C. and a barometric pressure of 770 mm. The corrected volume of dry air is therefore 18·9 c.c., the weight of which is $18{\cdot}9 \times 0{\cdot}001293 = 0{\cdot}0244$ gram. The vapour density of chloroform is then equal to $\frac{0{\cdot}1008}{0{\cdot}0244} = 4{\cdot}13$ compared with air, or $4{\cdot}13 \times 14{\cdot}39 = 59{\cdot}4$ compared with hydrogen, the molecular weight being accordingly 118·8, which agrees closely with 118·5, the number calculated from the formula $CHCl_3$.

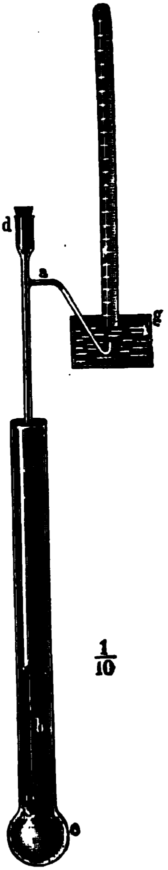

FIG. 23.

III. DETERMINATION OF THE MOLECULAR WEIGHTS OF SUBSTANCES IN SOLUTION.

74 The fact that the osmotic pressure exerted by equal weights of different substances in dilute solution, the depression of the freezing-point of the solvent, the depression of the vapour-pressure, and the rise of the boiling-point all vary inversely as the molecular weights of the dissolved substances, renders it possible to ascertain the relative molecular weights of the substances by measuring any one of these four quantities.

The methods which have established themselves in practice are, however, limited, on account of experimental difficulties, to the freezing-point method of Raoult, and the boiling-point method elaborated by Beckmann, Landsberger, and others.

In order to carry out the method based upon the determination of the depression of the freezing-point a weighed quantity of a suitable solvent is placed in a glass tube, the latter surrounded by a freezing mixture, and the freezing-point of the liquid determined by means of an accurate thermometer, graduated to $\frac{1}{100}$ of a degree. An exactly weighed amount of the substance is then added, allowed to dissolve completely, and the freezing-point of the solution then carefully ascertained in the same way as before. The difference observed between these two temperatures (*d*) is the depression of the freezing-point produced by (*b*) grms. of the substance dissolved in (*a*) grms. of the solvent. From this is calculated the depression which would be produced by 1 grm. of the substance dissolved in 100 grms. of the solvent (D), which is equal to $\frac{d \times a}{b \times 100}$. If now the molecular depression is MD, it follows that the molecular weight of the substance in question (M) is given by the equation :

$$M = \frac{MD}{D} = \frac{MD \times b \times 100}{d \times a}.$$

Thus 1·35 grm. of carbon tetrachloride dissolved in 55 grms. of acetic acid lowered the melting-point of the latter from 16·750° to 16·132°, the depression being therefore equal to 0·618°. Since the molecular depression, MD, for acetic acid is 39, it follows that the molecular weight of carbon tetrachloride must be

$$\frac{39 \times 1{\cdot}35 \times 100}{55 \times 0{\cdot}618} = 154{\cdot}9.$$

This number agrees satisfactorily with that obtained by the vapour-density method, viz., 153.

75 The determination of molecular weight from the rise in the boiling-point of a liquid produced by a dissolved substance is based on precisely similar principles.[1] The boiling-point of the pure solvent is first determined and then that of the solution, and the calculation is carried out in a similar manner. Thus, to take an example, the molecular rise for alcohol (produced by dissolving 1 gram-molecule of any substance in 100 grms. of alcohol) is 11·4°. In an experiment it was found that when

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[1] Beckmann, *Zeit. physikal. Chem.* 1889, **4**, 532; 1890, **6**, 437; 1891, **8**, 223; 1902, **40**, 129; Will und Bredig, *Ber.* 1889, **22**, 1084. Landsberger, *Ber.* 1898, **31**, 458.

0·8665 grm. of mercuric chloride, $HgCl_2$, were dissolved in 6·84 grm. of alcohol, the boiling-point was raised 0·530°. Hence 1 grm. dissolved in 100 grms. of alcohol would raise the boiling-point $\frac{0·530 \times 1 \times 6·84}{0·8665 \times 100} = 0·4184°$.

The molecular weight of mercuric chloride is therefore, according to this experiment, $\frac{11·4}{0·4184} = 272$, a number which agrees well with that expressed by the formula, viz., 269.

The experimental difficulties in obtaining a constant boiling-point necessitate the use of a somewhat complicated apparatus, for the details of which the original papers or some work on physical chemistry must be consulted.[1]

The fact that electrolytes in aqueous solution show an anomalous behaviour renders it impossible to employ the methods described above for determining their molecular weights unless a complete study of the behaviour of each substance is made. Substances which give abnormal numbers when examined in aqueous solution often, however, yield normal results when their solutions in other solvents are examined.

PHYSICAL DETERMINATION OF THE ATOMIC WEIGHT OF MONATOMIC GASES.

76 The identity of atom and molecule (p. 77) has been ascertained in the case of mercury and of the gases of the helium group by a physical method which is of great importance, as it appears to provide an independent mode of ascertaining whether the molecule of an element contains one or more atoms, without any reference to the compounds of the element. When a gas is heated, the quantity of heat required to raise its temperature by a given amount (its *specific heat*) depends on the conditions under which the gas is maintained. If the gas be allowed to expand, its specific heat is found to be greater than when it is heated at constant volume. The difference between the two specific heats represents the amount of heat equivalent to the work which is done by the gas in expanding against the atmospheric pressure, and can readily be calculated. This being known, the specific heat at constant volume can be

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[1] See Walker, *Introduction to Physical Chemistry*, chap. xviii.

obtained by subtracting this quantity from the specific heat at constant pressure, and the result thus found agrees with that obtained by direct experiment.

For an ideal monatomic gas not only can the specific heat at constant volume be calculated from that observed at constant pressure, as just described, but, in addition to this, both the specific heat at constant volume and that at constant pressure can be calculated directly according to the kinetic theory of gases. The result of this calculation is that the ratio of these two (k) is 1·66. The ratio actually found for the elementary gases oxygen, hydrogen, nitrogen, and other gases which contain two atoms in the molecule is, however, about 1·4. The explanation of this discrepancy is that when two atoms are present in the molecule a portion of the heat is spent in producing relative motion between these two atoms, this being summed up as internal work. The heat taken up by such a gas as oxygen therefore may be considered as made up of, at least, three different fractions—H_t, that required to actually increase the mean kinetic energy of the molecule, which is the same for all gases; H_e, that equivalent to the work done by the gas expanding against external pressure, which is nearly the same for all gases; H_i, the amount equivalent to the internal work done in the molecule of the gas, which is different in different gases. The ratio between the two specific heats of a gas like oxygen may therefore be expressed by the fraction $\frac{H_t+H_i+H_e}{H_t+H_i}$, which is always less than $\frac{H_t+H_e}{H_t}$, the expression for a monatomic gas.

The ratio between the two specific heats can be experimentally ascertained by measuring the velocity of sound in the gas in question, and then applying the equation $u=\sqrt{kg\frac{p}{d}}$ (where u is the velocity of sound in the gas, p the pressure, d the density, g the intensity of gravity, and k the ratio of the two specific heats), which holds for sound-waves in gaseous media. Such an experiment carried out with mercury vapour by Kundt and Warburg[1] gave the value 1·66 for the ratio of the two specific heats. These investigators thereupon pointed out that this shows that no internal work is done when mercury vapour is heated, the most probable explanation being that the molecule of mercury does not contain two atoms but

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[1] *Pogg. Ann.* 1868, **135**, 337, 517.

only one. This supposition is quite in agreement with the conclusion to be drawn from the vapour-density of mercury and its atomic weight as determined from other considerations (Vol. II., 1897, p. 13 et seq.).

The gases of the helium group behave in a similar manner to mercury vapour, the ratio of specific heats determined by the above method being also 1·66.

No independent means of ascertaining the atomic weights of these gases is at present available (1904), and it is, therefore, impossible to say whether the absence of internal work is actually due to the identity of atom with molecule, as in the case of mercury, or to some other cause.

CHEMICAL NOMENCLATURE.

77 Nomenclature is the spoken language of chemistry, as notation is the symbolic written language of the science. With the progress of discovery chemical nomenclature has naturally undergone great and frequent changes. The ancients were acquainted with only seven metals, viz.:—gold, silver, copper, tin, iron, lead, and mercury. Of these the first six are mentioned by Homer; mercury was not known in his time, but mention is made of the liquid metal by authors living one century before Christ. These seven metals were originally supposed to be in some way connected with the seven heavenly bodies then known to belong to our system. To bright yellow gold the name of *Sol* was given; whilst white silver was termed *Luna*; copper, which had chiefly been obtained from the island of Cyprus and received its common name (cuprum) from this source, was likewise called *Venus*, after the protectress of the island. Tin was specially dedicated to *Jupiter*; iron to *Mars*, the god of war; whilst heavy dull lead was connected with *Saturn*; and the mobile quicksilver was called *Mercury*, after the active messenger of the gods. The alchemists not only invariably used these names, but employed the signs of the heavenly bodies as symbols for the metals, and many remnants of this practice are found to this day in all languages. Thus we still speak of "lunar caustic" for silver nitrate, "saturnine poisoning" for poisoning by lead, whilst the name mercury has become the common one of the metal. To come to later times we find that the language of the alchemists was always and designedly obscure and enigmatical, so

that their names for chemical compounds were not based on any principle, but even chosen for the sake of secrecy or deception, and therefore bore no relation to the substances themselves. From these fanciful terms the progress to a better state of things has been slow, and the changes which the names have undergone have been numerous, whilst the same substance has at one time frequently been designated by many distinct names, several of which are still in use.

Bodies were generally named and classed by the alchemists by virtue of certain real or fancied resemblances existing between their physical properties. Thus, bodies which can be obtained by distillation and are, therefore, easily volatile, were all termed *spirits*, so that alcohol (spirits of wine) was classed together with hydrochloric acid (spirits of salt), and these again with spirits of turpentine, although these three substances are chemically as different as any three substances well can be. In the same way, all viscid, thick liquids were termed *oils*, and thus sulphuric acid, or oil of vitriol, came to be placed in the same class as olive oil; whilst semi-solid bodies, such as antimony trichloride, were termed *butters*, and considered to be analogous to common butter.

As soon as chemistry became a science, the nomenclature assumed a more scientific character. Some of the terms which came into use during the growth of the science have been mentioned in the Historical Introduction. These terms have by degrees been much changed, and such revolutions have accompanied the progress of the science, that at present the same compound is not unfrequently designated by different names. Thus it is clear that our nomenclature has not yet attained a permanent form; the names of chemical substances are not identical in different languages, and even in the same language, difference of practice in naming compounds is found among chemists. Nevertheless, we are guided by certain specific rules, and the science no longer suffers from the arbitrary nomenclature which the descriptive natural sciences have to endure.

78 The foundation of the modern system of chemical names was laid by Lavoisier and his colleagues,[1] and the plan proposed by them has been maintained, with slight modifications, up to the present time. The principle upon which our system

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[1] *Méthode de Nomenclature Chimique*, proposé par MM. de Morveau. Lavoisier, Berthollet, et de Fourcroy. Paris, 1787. Translated into English by Pearson. Second edition, 1799.

(for Inorganic Chemistry at least) is founded is, that every compound being made up of two or more elementary bodies united in different proportions, the name of that compound shall signify the nature of its elementary constituents, and as nearly as possible the relative proportions in which they are believed to be present. In the case of the carbon compounds (Organic Chemistry) it was soon found impossible, from the large number of closely-allied substances, uniformly to apply this system, and names suggested by the origin of the bodies have been in many cases adopted.

No special rule has been applied to the nomenclature of the elements. The old common names of those which have long been known have in most cases been retained, and when new elements have been discovered they have been named according to no pre-arranged plan. Some are named from the locality in which they have first been found; some from a characteristic property or from the mode of their discovery; whilst the names of others, such as Gallium, Scandium, and Germanium, bear witness to the patriotism of their discoverers. By common consent the names of all recently discovered metals end in "*-ium*," as sodium, barium, vanadium. The names of a group of allied non-metallic elements end in "*-ine*," thus we have fluorine, chlorine, bromine, and iodine; those of another group of somewhat analogous non-metallic elements end in "*-on*," as boron, carbon, silicon; whilst those of two other non-metals, more nearly resembling the metals, end like the latter in "*-ium*," thus we have selenium and tellurium.

Lavoisier introduced the term "*oxyde*" to signify the combinations of oxygen with the other elements, and words with the same ending have been since employed to denote the simple combinations of two elements or groups of elements, thus:—

The compounds of	form	such as
Hydrogen	Hydrides	Phosphorus hydride.
Fluorine	Fluorides	Calcium fluoride.
Chlorine	Chlorides	Sodium chloride.
Bromine	Bromides	Magnesium bromide.
Iodine	Iodides	Lead iodide.
Oxygen	Oxides	Mercury oxide.
Sulphur	Sulphides	Zinc sulphide.
Selenium	Selenides	Potassium selenide.
Phosphorus	Phosphides	Calcium phosphide.
Carbon	Carbides	Iron carbide.

It frequently happens that a metal forms several distinct oxides or chlorides, in which the constituents are present in simple multiple proportions of their combining weights. In these cases it is usual to give to each compound a name indicating either the number of atoms of oxygen which we believe to be combined with one atom of metal, or the simplest relation which we suppose it possible to exist between the number of atoms of metal and oxygen in the molecule: thus the oxide believed to contain one atom of oxygen is termed the monoxide; that containing two atoms is the dioxide; whilst oxides containing three, four, or five atoms of oxygen are called trioxides, tetroxides, and pentoxides respectively. Sometimes the first oxide is termed the protoxide (πρῶτος, first), the second deutoxide (δεύτερος, second), the third trioxide (τρίτος, third), and the highest peroxide.

When the relation of metal to oxygen is that of 2 to 3, as in red hæmatite, Fe_2O_3, the Latin prefix *sesqui*, meaning one and a half, is used, and the oxide is termed a sesquioxide. The same mode of designation applies to the compounds of metals with sulphur, chlorine, &c.: thus we speak of iron sesquisulphide, or if we please, sesquisulphide of iron, Fe_2S_3; of antimony trichloride, or, if we prefer it, the trichloride of antimony, $SbCl_3$.

In the case of metals, such, for instance, as iron and mercury, which form two distinct series of compounds, one corresponding to a lower oxide, and another to a higher one, it is customary to use the endings "*-ous*" and "*-ic*" (introduced by Berzelius[1]) to denote the difference between the two sets of compounds. Thus we have the mercur*ous* and the mercur*ic* salts. Among others, mercur*ous* oxide, Hg_2O, mercur*ous* chloride, HgCl (commonly called calomel), mercur*ous* nitrate, $HgNO_3$; and, on the other hand, mercur*ic* oxide, HgO, mercur*ic* chloride, $HgCl_2$ (commonly called corrosive sublimate), mercur*ic* nitrate, $Hg(NO_3)_2$. In the same way we have the ferr*ous* salts (from *ferrum*, iron) corresponding to ferr*ous* oxide, FeO (also termed the monoxide), and the ferr*ic* salts corresponding to ferr*ic* oxide, Fe_2O_3.

The endings *-ous* and *-ic* are applied not only in the case of oxides and chlorides but also in that of acids. Thus sulphur*ous* acid, H_2SO_3, contains *less* oxygen than sulphur*ic* acid, H_2SO_4; nitr*ous* acid, HNO_2, less than nitr*ic* acid, HNO_3;

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[1] *Journ. de Physique*, Oct. 1811.

and carrying this distinction still further, the names of *salts* of acids ending in *-ous* terminate in *-ite*, whilst those derived from acids in *-ic* end in *-ate*; thus for example—

Nitr*ous* acid forms salts termed nitr*ites*.
Sulphur*ous* acid „ „ sulph*ites*.
Nitr*ic* acid „ „ nitr*ates*.
Sulphur*ic* acid „ „ sulph*ates*.

With respect to the nomenclature of *acids* and *salts* some difference of opinion has been expressed by chemists, and hence a certain amount of confusion exists in chemical writings. Lavoisier, when he devised the present scheme of chemical nomenclature, believed that it is oxygen (*ὀξύς*, acid, *γεννάω*, I produce) which gives to the bodies formed by combustion in the gas their acid characters, and hence the highest oxides of the metals and non-metals were termed *acids*, thus P_2O_5 was called phosphoric acid, CO_2 carbonic acid, CrO_3 chromic acid, &c. The ordinary well-known substances possessing acid properties, such as nitric acid, HNO_3, and sulphuric acid, H_2SO_4, were looked upon as hydrates of the anhydrous oxides or acids, N_2O_5 and SO_3, from which they may be obtained by the action of water, thus:—

$$N_2O_5 + H_2O = 2HNO_3$$
$$SO_3 + H_2O = H_2SO_4.$$

Acid bodies were, however, next discovered, such as hydrochloric acid, HCl, hydrofluoric acid, HF, and hydrocyanic acid, HCN, which contain no oxygen; and thus it appears that Lavoisier's notion that the presence of oxygen is alone necessary to form an acid is incomplete, and a more correct definition of an acid is that it is a hydrogen compound, in which the whole or a part of the hydrogen is capable of being replaced by a metal; in other words an acid is a hydrogen salt. Nitric acid, therefore, is hydrogen nitrate HNO_3, and by replacing the hydrogen by the metal potassium we obtain potassium nitrate or nitrate of potassium, KNO_3. Sulphuric acid is hydrogen sulphate, H_2SO_4, and either one or both the atoms of hydrogen can be replaced by potassium, giving rise, in the first instance, to a salt termed hydrogen potassium sulphate (formerly bisulphate of potash), $HKSO_4$, and in the second case to potassium sulphate (formerly termed sulphate of potash), K_2SO_4. Acids which contain one atom of hydrogen replaceable by metals are called monobasic, those containing two, dibasic, and those containing three, tribasic. Nitric acid, HNO_3, is a monobasic acid, sulphuric acid, H_2SO_4, a dibasic, and phosphoric acid, H_3PO_4, in which all the atoms of hydrogen can be replaced, a tribasic acid.

The anhydrous oxides (such as N_2O_5 and SO_3), from which the acids are derived, may be best termed *anhydrides* or *acid-forming oxides*, whilst the oxides which have the power of acting as *bases* and of forming salts when brought into contact with acids are termed *basic* oxides.

79 At the time when our nomenclature was invented all salts were supposed to be compounds of an *acid* and a *base*; and names were given which indicated the fact that when the acid and the base are brought together a neutral salt is produced; thus, if we add potash (the base) to sulphuric acid (the acid) a salt is formed to which the name *sulphate of potash* was given. Where the acid is combined with a heavy metallic oxide, as, for instance, when oxide of lead is dissolved in an acid such as nitric acid, the common name nitrate of lead, or more simply lead nitrate, does not exhibit the analogy between this salt and that obtained by adding nitric acid to potash and called nitrate of potash, and in order to assimilate these names some chemists termed the first nitrate of oxide of lead, corresponding to nitrate of potash (potash being oxide of potassium). Salts are now regarded as formed from acids by the substitution of hydrogen by a metal or radical, and it has become the practice to mention in the name of the salt not the base but the *metal* or *basylous group*, so that the similar names of lead nitrate and potassium nitrate become the designations of these compounds. Other chemists prefer to modify the termination of the name of the metal, making it an adjective, thus:—potassic nitrate; and as the common word *lead* does not lend itself to such adjective forms, they are compelled to use the Latin word and term the salt *plumbic nitrate*, but this practice is greatly to be deprecated, as it introduces a confusion between these terms and those which designate a higher state of oxidation (p. 134).

In this work no special system of nomenclature will be adopted to the exclusion of every other system. As a rule, however, the ordinary name of the metal will be retained for the salts, thus:—lead nitrate, zinc sulphate, potassium chloride. But this will not preclude the occasional use of the common terms, as nitrate or carbonate of soda, whilst such names as ferrous and ferric, mercurous and mercuric salts, will of course be employed.

We define an *acid* to be a hydrogen salt, and, therefore, HNO_3 will be, as a rule, termed nitric acid: the name hydrogen nitrate may sometimes be used. Bodies such as N_2O_5, SO_3, CrO_3, will not be termed *acids* but are referred to as *anhydrides* or *acid-forming oxides*. In some few instances the compound CO_2 may be mentioned as carbonic acid or carbonic acid gas, owing to the fact that it has for a long time been so called; but the systematic name by which it will be designated in these pages is carbon dioxide.

The following comparison of some of the older and common and the scientific and more modern names of important acids and salts may prove useful.

ACIDS.

Older and Common Name.	Formula.	Modern and Scientific Name.
Nitric acid	HNO_3	Hydrogen nitrate.
Nitrous acid	HNO_2	Hydrogen nitrite.
Sulphuric acid	H_2SO_4	Hydrogen sulphate.
Sulphurous acid	H_2SO_3	Hydrogen sulphite.
Chloric acid	$HClO_3$	Hydrogen chlorate.
Chlorous acid	$HClO_2$	Hydrogen chlorite.
Hypochlorous acid	$HClO$	Hydrogen hypochlorite.

SALTS.

Older and Common Name.	Formula.	Modern and Scientific Name.
Nitrate of potash	KNO_3	Potassium nitrate.
Nitrate of silver	$AgNO_3$	Silver nitrate.
Sulphate of lime	$CaSO_4$	Calcium sulphate.
Sulphite of lead	$PbSO_3$	Lead sulphite.
Chlorate of potash	$KClO_3$	Potassium chlorate.
Chlorite of soda	$NaClO_2$	Sodium chlorite.
Hypochlorite of potash	$KClO$	Potassium hypochlorite.
Protosulphate of iron	$FeSO_4$	Ferrous sulphate.
Perchloride of iron	$FeCl_3$	Ferric chloride.

This system of nomenclature is, however, by no means perfect, nor is it universally carried out. Were we to do so, long and inconvenient names would have to be used. Thus, instead of the common name alum, we should have to use the words potassium aluminium sulphate, and for bitter-spar the name calcium magnesium carbonate. Hence we shall often use the common instead of the strictly scientific names, as common salt for sodium chloride, caustic potash for potassium hydroxide, sulphuric acid for hydrogen sulphate, and nitre or saltpetre for potassium nitrate.

THE NON-METALLIC ELEMENTS

80 All the non-metallic elements except those of the helium group form volatile compounds with hydrogen, and if these be compared it is found that they fall into four classes; this is apparent in the following table, which contains the molecular formulæ of these compounds:

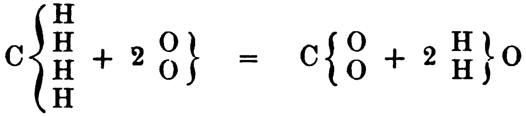
I.	Hydrogen. $\left.\begin{matrix}H\\H\end{matrix}\right\}$	Hydrofluoric acid. $\left.\begin{matrix}H\\F\end{matrix}\right\}$	Hydrochloric acid. $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	Hydrobromic acid. $\left.\begin{matrix}H\\Br\end{matrix}\right\}$	Hydriodic acid. $\left.\begin{matrix}H\\I\end{matrix}\right\}$
II.	Water. $\left.\begin{matrix}H\\H\end{matrix}\right\}O$	Sulphuretted Hydrogen. $\left.\begin{matrix}H\\H\end{matrix}\right\}S$	Seleniuretted Hydrogen. $\left.\begin{matrix}H\\H\end{matrix}\right\}Se$	Telluretted Hydrogen. $\left.\begin{matrix}H\\H\end{matrix}\right\}Te$	
III.	Ammonia. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	Phosphuretted Hydrogen. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$	Arseniuretted Hydrogen. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$	Hydride of Boron. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}B$	
IV.		Marsh Gas. $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$	Siliciuretted Hydrogen. $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}Si$		

It appears from this that the elements differ in their behaviour, one atom of some of them combining with one atom of hydrogen, whilst an atom of others combines with two atoms of hydrogen, and others again with three and four. Each element therefore possesses a certain combining power or *valency* as it is called.

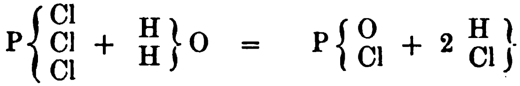
The elements of the first group in the preceding table are said to be monovalent, those of the following groups being divalent, trivalent, and tetravalent. This is also sometimes expressed by saying that the elements of the first group are monads, and those of the succeeding ones dyads, triads, and tetrads. So long as we only examine the compounds of the non-metals with hydrogen, the relations are simple and definite; but when the comparison is extended to their compounds with other elements, it is found that the valency does not possess a constant value. Phosphorus, for example, combines with chlorine in two different proportions, producing the compounds phosphorus trichloride, PCl_3, and phosphorus pentachloride, PCl_5, in the first of which one atom of phosphorus is united with three atoms of chlorine, whilst in the second it is combined with five. It is true that when the latter of these substances, PCl_5, is heated, it is decomposed into the simpler molecules PCl_3 and Cl_2, and hence the conclusion was at one time drawn that the combination between the molecules PCl_3 and Cl_2, to form PCl_5, differs in some way from that between the atoms of phosphorus and chlorine to form PCl_3. Substances of this kind, which cannot be vaporised without decomposing into simpler molecules, were then called molecular compounds, and the valency of an element measured by the number of atoms of monad elements combining with it to form a compound vaporising without decomposition. The whole question turns upon the molecular weights of the compounds under discussion, and although phosphorus pentachloride cannot be vaporised without decomposition, it is found that in solution its molecular weight does correspond to the formula PCl_5. In the light of our present knowledge, therefore, these distinctions cannot be maintained, and the valency of the elements must be looked upon as a variable quantity. A more definite value appears to attach to the maximum valency displayed by the elements in particular classes of compounds, which can be ascertained from the molecular formulæ of their compounds, but even this is subject to exceptions. (Vol. II. (1897) pp. 28–37.)

Elements which are of equal valency combine with and replace one another atom for atom, whilst one atom of a divalent element can replace or combine with two monovalent atoms, and a trivalent atom either three monovalent or one mono- and one divalent atom, as is seen in the following equations:

$$2\,HI + Cl_2 = 2HCl + I_2$$



$$C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right. + 2\left.\begin{matrix}O\\O\end{matrix}\right\} = C\left\{\begin{matrix}O\\O\end{matrix}\right. + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O$$



$$P\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. + \left.\begin{matrix}H\\H\end{matrix}\right\}O = P\left\{\begin{matrix}O\\Cl\end{matrix}\right. + 2\left.\begin{matrix}H\\Cl\end{matrix}\right\}$$

81 A careful study of the chemical properties of substances teaches that in many cases special relations exist between the different atoms of which the molecule is made up, and these may be expressed in formulæ which are known as *constitutional* formulæ. The properties of many oxy-acids, for instance, show that their hydrogen atoms stand in a special relation to some of their oxygen atoms. This is expressed in the following constitutional formulæ for some of the commoner acids:

Nitric acid	$HO.NO_2$.
Sulphuric acid	$(HO)_2SO_2$.
Phosphoric acid . . .	$(HO)_3PO$.
Iodic acid	$HO.IO_2$.

The group or radical (HO) which appears in all these formulæ is known as the hydroxyl group and behaves as a monovalent radical, since, although it is not known in the free state, it is found in water and other compounds combined with or replacing a monovalent atom.

It is only after the constitution of a compound has been ascertained that it is possible to determine the valency of the atoms of which it is composed. Thus the formula of iodic acid, HIO_3, might be either that given above or

H.O.O.O.I.

In the former case, which seems to be the more probable, the atom of iodine, being directly combined with two divalent atoms and a monovalent group, would be pentavalent, whilst in the latter it would be monovalent.

HYDROGEN. H = 1 (O = 15·88) = 1·008 (O = 16)

82 It has already been stated (see Historical Introduction) that water was long supposed to be an elementary or simple substance, and it was not until the year 1781 that Cavendish proved that water was produced by the union of oxygen and hydrogen gases, whilst Humboldt and Gay-Lussac first showed in 1805 that these gases combine by volume in the simple relation of one to two. Turquet de Mayerne at the commencement of the seventeenth century had indeed obtained an inflammable gas by the action of dilute oil of vitriol on iron, but the true nature of this gas was first ascertained by Cavendish in 1766,[1] when he showed that hydrogen was a peculiar gas to which he gave the name of "inflammable air."

Terrestrial hydrogen occurs almost solely in a state of combination, although it has been found to exist in the free state mixed in small quantities with other gases in certain volcanic emanations,[2] and also in very small quantity in the atmosphere.[3] It has further been found by Graham as occluded gas in the meteoric iron from Lenarto,[4] and by Mallet in a meteorite from Virginia.[5] It is produced in the decay and decomposition of various organic bodies, being found in the intestinal gases of many animals, as also, according to Sadtler, in the gases given off by the oil-wells of Pennsylvania.

In a state of combination hydrogen occurs in water, of which it constitutes very nearly one ninth part by weight (exactly 11·19 per cent.), and from this it derives its name (ὕδωρ, water; and γεννάω, I give rise to). Hydrogen likewise occurs in nature, though in smaller quantities, combined with sulphur, phosphorus, chlorine, bromine, iodine, and nitrogen, whilst it forms an essential portion of nearly all organic substances.

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[1] "Experiments on Factitious Air," *Phil. Trans.*, 1766, p. 144.

[2] Bunsen, *Pogg. Ann.*, 1851, **83**, 197. Ch. St. Claire Deville, *Compt. Rend.*, 1862, **55**, 75.

[3] Gautier, *Ann. Chim. Phys.* 1901 [7], **22**, 5; Dewar, *Proc. Roy. Soc.*, 1901, **68**, 360.

[4] *Proc. Roy. Soc.*, 1867, **15**, 502.

[5] *Proc. Roy. Soc.*, 1872, **20**, 365.

83 *Preparation.*—(1) Pure hydrogen is prepared by the electrolysis of acidulated water. For this purpose a mixture of one part by weight of pure sulphuric acid with ten parts of water is placed in the glass decomposing cell (Fig. 24). The positive pole consists of a platinum wire (*a*) melted through the glass and placed in contact with mercury amalgamated with zinc (*b*), whilst the negative pole (*c*) is composed of a platinum plate. When the current from two or three of Bunsen's elements is passed through the apparatus a constant stream of pure hydrogen is evolved, and after being washed by the small quantity of sulphuric acid contained in the bulbs (*d*), the gas may be collected for analytical purposes. The oxygen of the water is all absorbed by the zinc amalgam, oxide of zinc and ultimately zinc sulphate being formed, whilst the whole of the hydrogen is evolved in the pure state. Instead of dilute sulphuric acid, dilute solutions of caustic potash or soda are frequently employed; according to H. B. Baker,[1] a solution of thoroughly purified barium hydroxide must be employed if the highest degree of purity is required.

FIG. 24.

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[1] *Journ. Chem. Soc.*, 1902, 400.

(2) When metallic palladium is exposed to the impure hydrogen gas formed by any of the methods described below, it absorbs large quantities of the gas (p. 150), and when the resulting substance is heated in a vacuum, the hydrogen is evolved in a state of purity.

(3) By acting on water with the alkali metals, or with an amalgam of sodium or potassium, the metal replaces an equivalent quantity of hydrogen in the water, hydrogen gas and the soluble hydroxide of the metal being formed thus:

$$K_2 + 2H_2O = 2KHO + H_2.$$

When a small piece of potassium is thrown into a basin of water, it swims about on the surface with a hissing noise, and bursts into flame; this is due to the fact that the metal in uniting with the oxygen of the water evolves heat enough to melt the metal and to ignite the liberated hydrogen, which then burns with a flame coloured violet by the presence of the vapours of the metal. Sodium, likewise, decomposes water, but the hydrogen in this case does not take fire spontaneously unless the water be hot, or the motion of the bead of metal be checked, as when the metal is thrown on to a viscid starch-paste or on to a moistened sheet of blotting-paper, in which cases the movement of the molten globule is so retarded that the metal becomes hot enough to cause the ignition of the hydrogen, which then burns with the yellow flame characteristic of the sodium compounds. If the blotting-paper be previously stretched upon an inclined wooden tray and moistened with a red solution of litmus, the track of the molten potassium or sodium, as it runs over the paper, will be seen by a blue line showing the formation of an alkaline product. In order to collect the hydrogen thus evolved, the small clean globule of sodium may be caught and depressed below the surface of the water by means of a little sieve of wire-gauze under the open end of a cylinder[1]; the bubbles of gas then rise and may be collected, as shown in Fig. 25. Hydrogen may also be prepared by passing steam over metallic sodium.

(4) By passing steam over red-hot iron wire or iron borings placed in an iron tube and heated in a furnace, as shown in Fig. 26, *a* being a retort in which water is boiled. The iron

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[1] Explosions may ensue if the sodium adheres to the glass.

is converted into the black or ferrosoferric oxide, Fe_3O_4, and hydrogen is evolved, thus:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

(5) The most convenient mode of preparing hydrogen gas for ordinary use where absolute purity is not requisite, is by the action of sulphuric acid, diluted with six to eight times its weight of cold water, upon metallic zinc; the addition of water is necessary, inasmuch as concentrated acid has no action on the metal in the cold, but dissolves it on heating with evolution of sulphur dioxide. If the metallic zinc is quite pure, it is hardly attacked by the dilute acid, owing to the formation of a film of hydrogen gas on the surface of the metal, which protects it from the further action of the acid. When impurities are present which are more electro-negative than zinc, galvanic action takes place, the hydrogen being then evolved from the electro-negative substance, leaving the zinc surface exposed to the further action of acid. Where pure zinc is used a few drops of copper sulphate or platinum chloride solution are therefore added, which results in the deposition of the electro-negative copper or platinum on the zinc, the evolution of hydro-

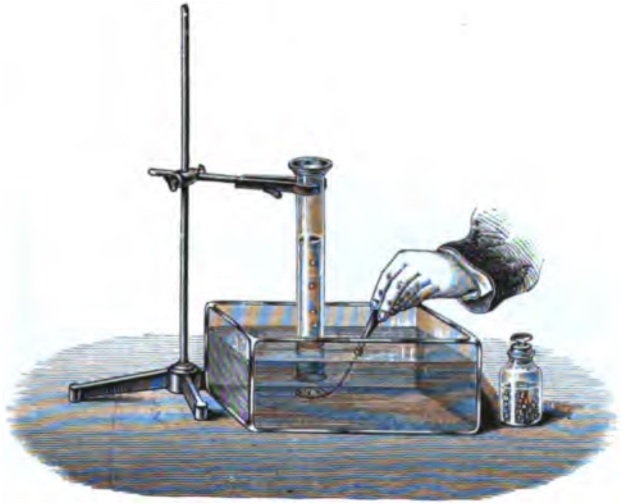

FIG. 25.

gen then taking place readily. Hydrochloric acid diluted with twice its weight of water may also be employed, and poured upon clippings of metallic zinc contained in a gas-generating bottle. Other metals, such as iron, may be used instead of zinc, and magnesium is sometimes employed where a very pure gas is required. The acid is gradually poured upon the metal by means of the tube funnel, and the evolved gas can be collected in cylinders over the pneumatic trough as shown in Fig. 27. The above reactions are represented as follows:

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$
$$2HCl + Zn = ZnCl_2 + H_2.$$

Care must be taken that all the air is expelled from the flask before the gas is collected, and in order to ensure freedom from air the gas is first allowed to fill an inverted test-tube, which is then brought mouth downwards to a flame; if the hydrogen burns quietly all air has been expelled, if it burns with a slight explosion the evolution must be allowed to continue before the gas is collected.

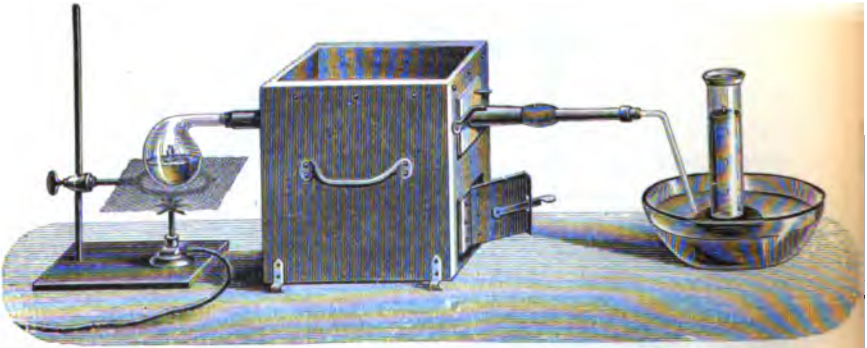

FIG. 26.

Hydrogen thus prepared always contains small quantities of impurities derived from the materials used; these can be got rid of by passing the gas through various absorbents. Of these impurities the most common are arseniuretted hydrogen, when the zinc, iron, or acid contains arsenic; phosphuretted hydrogen, when they contain phosphorus; nitrous fumes when the acid contains nitric acid or nitrates; sulphur dioxide and sulphuretted hydrogen when these gases are contained in the acid or when hot, even diluted, sulphuric acid is allowed to come in contact with the metal.

In order to purify the gas, the best method is to pass it through two U-tubes, each one metre in length, filled with broken glass; in the first tube the glass is moistened with an aqueous solution of lead nitrate, which absorbs the sulphuretted hydrogen; the second tube contains an aqueous solution of silver sulphate, by which the arseniuretted and phosphuretted hydrogen gases are arrested. After this the gas is passed through a third tube containing pumice moistened with a strong solution of caustic potash; then through two others, one containing pumice moistened with strong sulphuric acid, and the other phosphorus pentoxide, by means of which the gas is thoroughly dried. When absolute purity is aimed at the use of sulphuric acid for drying the gas has to be discontinued, since sulphur dioxide is formed in small quantity when hydrogen is dried in this way.

Fig. 27.

When the hydrogen is evolved from metallic iron, or even from impure zinc, the gas possesses a very unpleasant smell, due to the presence of small quantities of volatile hydrocarbons derived from the carbon contained in the metal. The best way of removing this odour is to pass the hydrogen through a tube filled with small pieces of charcoal, a substance which absorbs the hydrocarbons. Another impurity which it is much more difficult to remove from hydrogen is atmospheric air. This is partly contained dissolved in the liquids used in the preparation of the gas, but its presence may also be due to the high diffusive power of hydrogen, which causes it to escape through the pores of the cork and caoutchouc, whilst at the same time a certain quantity of air diffuses into the apparatus. In order to free the hydrogen from traces of oxygen, the gas must be passed through a red-hot tube filled with metallic copper, and then the water, produced by the combination of the oxygen and hydrogen, absorbed by passing the gas over phosphorus pentoxide. The nitrogen of the air cannot be got rid of, so that its presence must be prevented by a careful air-tight construction of the apparatus.

(5) Strong aqueous solution of potash dissolves metallic zinc, hydrogen being liberated, and a compound of zinc oxide and potash, K_2ZnO_2, being formed. This process yields an inodorous gas:

$$2KHO + Zn = H_2 + K_2ZnO_2.$$

Aluminium may also be used in place of zinc.

84 *Properties.*—Hydrogen is a colourless, tasteless, inodorous gas; it is the lightest substance known, being 14·39 times as light as atmospheric air, and has therefore a density of 0·06949 (air = 1). By carefully weighing a glass globe, first empty, and then filled with air and hydrogen, Regnault found that 1 litre of hydrogen at 0° and under a pressure of 760 mm. of mercury weighs, at the latitude of Paris, 0·089578 gram; he omitted, however,[1] to make a correction for the compression of the glass vessel when vacuous by the external atmospheric pressure, and if this correction be introduced his results show that the litre of hydrogen weighs 0·089894 gram under the above conditions. As the result of a long series of determinations conducted with the greatest care, E. W. Morley[2] has found that at sea-level in the 45th degree of latitude under normal conditions of temperature and pressure 1 litre of the pure gas weighs 0·089873 gram, and that 1 gram of hydrogen under the same conditions occupies 11·126 litres. As already pointed out (p. 84), the volume occupied by a given mass of gas varies at different

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[1] Rayleigh, *Proc. Roy. Soc.*, 1888, **43**, 356; Crafts, *Compt. Rend.*, 1888, **106**, 1662.

[2] *Zeit. physikal. Chem.*, 1896, **20**, 242.

places on the earth's surface, owing to the variations in the intensity of gravitation, and, as a rule, the figures given refer to the conditions at Paris. For that locality 1 litre of hydrogen weighs 0·089901 gram, and 1 gram occupies 11·1235 litres.

Hydrogen was first liquefied in 1884 by Wroblewski,[1] who cooled the gas under a pressure of 190 atm. by means of boiling nitrogen, and then quickly lowered the pressure to 1 atm., a grey, foam-like mass being thus obtained. Olszewski[2] in the same year compressed the gas to 180 atm. in a glass tube 2 mm. in diameter, simultaneously cooling it with liquid air boiling in vacuo. On suddenly reducing the pressure to 40 atm., he obtained colourless drops of liquid. Dewar[3] first succeeded in preparing the liquid in sufficient bulk to show a definite meniscus, by taking advantage of the Joule-Thomson cooling effect (p. 108).

In his experiments, hydrogen cooled to − 205° and under a pressure of 150 atm. was allowed to escape continuously from the nozzle of a coil of pipe at the rate of 10—15 cubic feet per minute, in a vacuum vessel of special construction, surrounded with a space kept below − 200°. Liquid hydrogen then commenced to drop from this vacuum vessel into another which was doubly isolated by being surrounded with a third vacuum vessel, 200 c.c. of liquid hydrogen being obtained in about five minutes.

Liquid hydrogen forms a clear colourless liquid, boiling at − 252·5° (as measured by a helium thermometer); it has a density of 0·700 at its boiling point, and is therefore much the lightest liquid known. Its specific heat is about 6, so that hydrogen follows Dulong and Petit's law (Vol. II. (1897) p. 15), and has a greater specific heat than any other known substance. When the liquid is cooled by rapid evaporation, it forms a colourless solid melting at − 257° according to Dewar, or at − 258·9° according to Travers,[4] and has a specific gravity of 0·0763 at − 259·9°.[5] The critical pressure of hydrogen is about 15 atm. and the critical temperature about − 243 to − 241° (Dewar).

The statement of Pictet[6] that hydrogen condenses to a steel-

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[1] *Compt. Rend.*, 1884, **100**, 979.

[2] *Compt. Rend.*, 1884, **99**, 133; 1885, **101**, 238.

[3] *Proc. Chem. Soc.*, 1895, 229; *Journ. Chem. Soc.*, 1898, 528; *Proc. Roy. Soc.*, 1901, **68**, 360; see also Travers, *Phil. Mag.*, 1901 [6], **1**, 411.

[4] *Proc. Roy. Soc.*, 1902, **70**, 484.

[5] *Proc. Roy. Soc.*, 1904, **73**, 251.

[6] *Ann. Chim. Phys.*, 1878 (5), **13**, 145.

blue liquid which by rapid evaporation yields solid particles of the same colour has since proved to be erroneous. The physical properties of the liquid and solid do not show any resemblance to those of the metals.

Hydrogen is an inflammable gas taking fire when brought in contact with a flame, and combining with the oxygen of the air to form water; it does not support ordinary combustion or animal life; when pure it may be breathed without danger for a short time, but it produces a singular effect upon the voice, weakening it and rendering it of higher pitch. On combining with 7·94 grams of oxygen to form water, one gram of hydrogen evolves heat sufficient to raise 33,950 grams of water from 0° to 1° Centigrade, and this is termed the *calorific power* of hydrogen, which is, therefore, equal to 33,950 *thermal units* or *calories*.

Hydrogen gas is very slightly soluble in water, 1 c.c. of the latter dissolving only 0·021 c.c. at 0·5°; the numbers obtained by Bunsen appeared to show that the solubility of hydrogen remained constant between 0° and 20°, but this has proved on further investigation to be incorrect. The absorption coefficient between 0° and 20° is given by the following interpolation formula:[1]

$$C = 0{\cdot}02148 - 0{\cdot}0002215t + 0{\cdot}00000285t^2.$$

Hydrogen is somewhat more soluble in alcohol than in water and its solubility diminishes with the temperature. The following interpolation formula gives the absorption coefficient (C) in alcohol for temperatures from 0° to 25°:—

$$C = 0{\cdot}06925 - 0{\cdot}0001487t + 0{\cdot}000001t^2.$$

85 *Absorption of Hydrogen by Metals.*—In 1863 Deville and Troost[2] observed that hydrogen has the power of diffusing through red-hot platinum and iron, but not through the cold metals, and suggested, as an explanation of the phenomenon, that it was caused by the greater porosity of the metals in the heated state. The subject was then further investigated by Graham,[3] who found that palladium possessed the same property in a much higher degree; the rate at which the hydrogen permeates this metal is such that through a surface

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[1] Winkler, *Ber.*, 1891, **24**, 98; Timofejew, *Zeit. physikal. Chem.*, 1890, **6**, 141.

[2] *Compt. Rend.*, 1863, **57**, 894.

[3] *Proc. Roy. Soc.*, 1867, **15**, 223; 1868, **16**, 422; 1869, **17**, 212, 500.

of 1 sq. metre 3992·22 c.c. of the gas pass each minute, whereas the rate of permeability through the same surface of platinum is 489·2 c.c., and through a sheet of caoutchouc of the same thickness and area it is represented by the passage of 127·2 c.c. in the same time.

Graham showed further that there is no need to assume a porosity in the structure of the metals to account for this phenomenon, but that it is due to the fact that such metals absorb the hydrogen-yielding substances which still retain characteristic metallic properties, but readily evolve part of the absorbed gas under altered conditions; the last traces of the gas can, however, only be driven off at a red heat in vacuo. This property may be examined in the following manner: A known weight of palladium foil or wire is placed in a small porcelain tube, glazed inside and out, which can be evacuated completely by a Sprengel vacuum pump (Fig. 28). The tube is first

FIG. 28.

exhausted, and hydrogen then allowed to pass over the metal, which is first heated and then allowed to cool in the hydrogen atmosphere, when it absorbs the gas in large quantity. The amount of hydrogen absorbed may be measured by evacuating the tube, and then heating in vacuo until no more hydrogen is evolved, the latter being all collected over mercury and measured.

The amount of hydrogen absorbed depends to some extent on the physical condition of the metal; in one experiment a palladium wire was found by Graham to absorb 935 times its volume of hydrogen, and increased in length from 609·14 mm. to 618·91 mm., or 1·6 per cent. In another experiment the metal showed an increase of bulk of 9·827 per cent. More recent experiments by Mond, Ramsay, and Shields[1] have shown that palladium black absorbs at the ordinary temperature 873—889 volumes of hydrogen, after allowing for the volume which combines with the oxygen invariably present in the black, and that palladium sponge and wire under proper conditions absorb a similar amount. When the palladium-hydrogen thus formed is subjected to a vacuum it readily evolves hydrogen; the substance obtained from the black loses 98 per cent. of the total hydrogen at the ordinary temperature, and the remainder almost completely at 444°, whilst the substance obtained from the foil loses but little hydrogen until the temperature reaches 100°, when the great bulk of it is evolved. In all cases a dull red heat is required to drive off the last traces. Under very high pressures, however, palladium is still capable of absorbing large quantities of hydrogen even at a red heat, Dewar[2] having shown that 300 volumes are absorbed at 500° under a pressure of 120 atmospheres.

Graham likewise found that when palladium is employed as negative electrode in the electrolysis of water, it very readily unites with hydrogen, absorbing 935 volumes, the expansion being proportional in all directions to the amount of hydrogen absorbed. If the electrolysis is continued after the above point is reached, the palladium becomes supersaturated with hydrogen, the limit of supersaturation varying with the strength of the current; the excess of hydrogen is, however, evolved directly the current ceases.[3]

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[1] *Phil. Trans.*, 1898, A **191**, 105.

[2] *Proc. Chem. Soc.*, 1897, 192.

[3] Thoma, *Zeit. physikal. Chem.*, 1889, **3**, 69.

Platinum foil was found by Graham to absorb 3·8 times its volume of hydrogen at a red heat, and 0·76 volume at 100°. Mond, Ramsay, and Shields[1] have found that at 550° platinum black absorbs slightly over 100 volumes of the gas, which is partly evolved in vacuo at the ordinary temperature. Iron, nickel, cobalt, gold, and copper also absorb small quantities of hydrogen.

The exact nature of the substances which are formed in this manner has not yet been ascertained with certainty. The appearance of the metals does not undergo change after absorption of hydrogen, and the specific gravity, conductive power for heat and electricity, and tenacity, although somewhat diminished, are affected to a much smaller degree than would probably be the case by combination with any other non-metallic substance. Graham concluded that the hydrogen does not chemically combine with the metal, but rather assumes the solid form and acts as a quasi-metal, giving rise to a kind of alloy, such, for instance, as is obtained when sodium and mercury are brought together, and this hypothesis is supported by the fact that in many of its chemical properties hydrogen is much more nearly allied to the metals than to the non-metals. To this absorbed form of hydrogen he gave the name *Hydrogenium*, and for the property of these metals to absorb the gas without loss of their characteristic metallic properties he proposed the term "occlusion" (from *occludo*, I shut up).

From the expansion of alloys of palladium with platinum, gold, and silver, when charged with hydrogen, Graham calculated the specific gravity of hydrogenium to be 0·733, but subsequent determinations by Dewar gave the figure 0·620. It was thought by many chemists that when hydrogen was liquefied and solidified it would itself possess metallic properties in those states, but the successful accomplishment of this problem by Dewar has shown that such is not the case, the liquid and solid having no resemblance to the metals (p. 150). The specific gravity of solid hydrogen at −259·9° is moreover only 0·076, or about one-eighth of that found by calculation for the hydrogen absorbed by palladium, and it would therefore appear probable that if hydrogen is absorbed without chemical combination it must have in the occluded state a different allotropic form from that in which it is obtained by liquefaction.

In opposition to Graham, Troost and Hautefeuille[2] believed

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[1] *Phil. Trans.*, 1895, A **186**, 657 ; 1897, A **190**, 129.

[2] *Compt. Rend.*, 1874, **78**, 686.

that in palladium-hydrogen a definite compound of the two elements of the formula Pd_2H was formed, which was capable of absorbing further quantities of hydrogen, whilst others have suggested the existence of the compound Pd_3H_2. The renewed investigation of the subject by Hoitsema[1] has however shown that at temperatures varying from 20° to 200° the relation of the vapour pressure of palladium-hydrogen containing varying quantities of hydrogen, to the atomic ratio in which the hydrogen and palladium are present, is what would be expected if the substance was simply a mixture of two non-miscible solid solutions of hydrogen in the metal, the miscibility of which, however, increases with rise of temperature: the curves thus obtained do not show any breaks indicating the existence of definite compounds.[2]

The metals lithium, sodium, potassium, and calcium also unite with hydrogen, but the products formed are entirely different from those described above, being well-defined crystalline substances having the formulæ LiH, NaH, KH, and CaH_2,[3] and possessing no metallic properties. The compounds Na_2H and K_2H, described in 1874 by Troost and Hautefeuille[4] as possessing metallic properties, appear in the light of Moissan's results to require fresh investigation.

The meteoric iron of Lenarto,[5] containing 90·88 per cent. of iron, yields when heated in vacuo 2·85 times its volume of a gas consisting almost entirely (85·68 per cent.) of hydrogen. This, coupled with the fact that under the ordinary pressure iron absorbs only about half its volume of hydrogen, would appear to show that the Lenarto meteorite has come from an atmosphere containing hydrogen under a pressure much greater than that of our own atmosphere, and thus we obtain an unexpected confirmation of the conclusions drawn from spectroscopic observations by Huggins, Lockyer, and Secchi respecting the existence of dense and heated hydrogen atmospheres in the sun and fixed stars.

The spectrum of hydrogen consists essentially of four bright

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[1] *Zeit. physikal. Chem.*, 1895, **17**, 1.

[2] For a further discussion of the subject and a complete list of the literature relating thereto, see E. Bose, *Zeit. physikal. Chem.*, 1900, **34**, 701; also Findlay, *The Phase Rule* (Longmans, 1904), p. 176.

[3] Guntz, *Compt. Rend.*, 1896, **122**, 244; Moissan, *Compt. Rend.*, 1902, **134**, 18, 71.

[4] *Compt. Rend.*, 1874, **78**, 968.

[5] Graham, *Proc. Roy. Soc.*, 1867, **15**, 502.

lines—one in the red, identical with Fraunhofer's dark line C, and one in the greenish blue coincident with the dark line F. The wave-lengths of these four lines, according to Angström's measurements, are, C = 6562, F = 4861, Blue = 4340, and Indigo = 4101 (in 10 millionths of a millimetre).

86 *Experiments with Hydrogen.*—The following experiments show that hydrogen is a very inflammable gas, burning with a nearly colourless flame, but incapable of supporting ordinar combustion :—

FIG. 29.

(1) When a lighted taper is brought to the open end of a cylinder filled with hydrogen, the gas will burn slowly and quietly if the open end be held downwards, but quickly and with a sudden rush of flame if the gas be allowed to escape by holding the mouth of the jar upwards.

(2) That hydrogen does not support the combustion of a taper may be shown by thrusting a burning taper into a jar of

hydrogen held with its mouth downwards; the gas inflames and burns round the open end of the cylinder, but the taper goes out and may be rekindled on withdrawal at the flame of burning hydrogen.

(3) The stream of gas issuing from the drawn-out end of a tube and furnished with a platinum nozzle attached to the generating flask may be ignited, care being taken that all the air has previously been expelled, when the flame will burn with a quiet and almost colourless flame.

(4) Owing to the lightness of hydrogen it may be collected by upward displacement. A jar filled with air is placed over the tube by which the gas escapes from the generating flask; in a short time the lighter gas will have displaced (Fig. 29) the heavier air, and the jar is then found to be full of hydrogen.

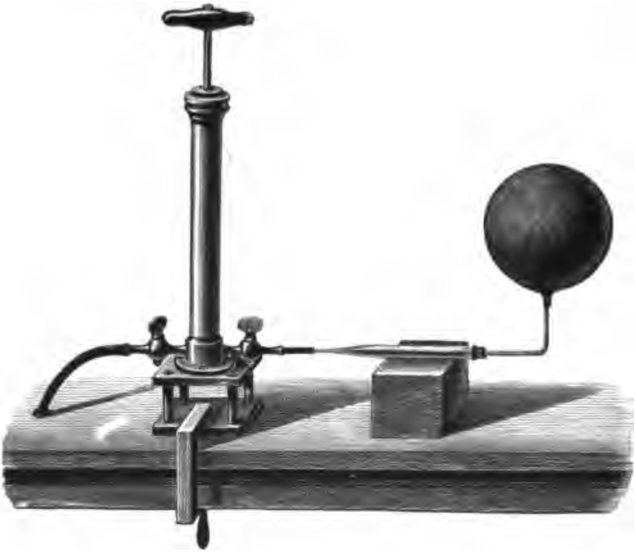

Fig. 30.

(5) Another striking mode of showing the relative weight of air and hydrogen has already been described in Fig. 3, page 46. The suspended beaker-glass is equipoised by weights placed in the pan at the other end of the beam of the balance, and the air is then displaced by pouring upwards the hydrogen contained in a large cylinder. The beam will no longer be horizontal, and weights must be placed on the beaker-glass to restore the equilibrium.

(6) Another experiment illustrating the same property of hydrogen is to fill a cylinder with the gas and to bring it mouth downwards, together with another cylinder filled with air, also mouth downwards; by gradually lowering the end of the hydrogen cylinder until the two cylinders come mouth to mouth, the hydrogen will be found in the upper cylinder, whilst on standing for a moment or two the lower one will be found to be full of air.

(7) Soap bubbles or small collodion balloons ascend when filled with hydrogen gas; the caoutchouc balloons now so common are filled and expanded by forcing hydrogen in with a syringe, as seen in Fig. 30. In consequence of its low specific gravity, hydrogen is sometimes employed for inflating balloons, but at present coal gas is generally used for this purpose.

THE HALOGENS

FLUORINE. $F = 18{\cdot}9 \quad (H = 1)$
$= 19{\cdot}0 \quad (O = 16)$

87 **Fluorine** occurs not uncommonly combined with calcium, forming the mineral fluor-spar, or calcium fluoride, CaF_2, crystallising in cubes and octahedra, and found in Derbyshire, the Harz, Bohemia, and elsewhere. It is likewise contained in other minerals, such as cryolite, a fluoride of aluminium and sodium ($3\,NaF + AlF_3$), found in Greenland, and occurs in smaller quantities in fluor-apatite, yttrocerite, topaz, lepidolite, &c. Fluorine has been detected in minute traces in sea-water and in the water of many mineral springs. Nor is its presence confined to the mineral kingdom, for it has been found in the enamel of the teeth as well as in the bones of mammalia, both fossil and recent, and it is said to have been detected in the blood, in the brain, and in milk.

The fact that glass can be etched when it is exposed to the fumes arising from fluor-spar heated with sulphuric acid, was known towards the latter part of the seventeenth century. Scheele first stated that fluor-spar was the calcium salt of a peculiar acid, which he obtained in an impure state by distilling a mixture of sulphuric acid and fluor-spar in a tin retort. Scheele also prepared the gaseous tetrafluoride of silicon, SiF_4, by the action of the acid thus produced upon silica. It is, however, to the researches of Gay-Lussac and Thénard[1] that we are indebted for the first reliable information concerning hydrofluoric acid. The views then held concerning this compound were incorrect, inasmuch as it was supposed to contain oxygen, and termed fluoric acid, until Ampère in 1810, and subsequently Davy, showed that this acid is analogous to hydrochloric acid, and that fluor-spar, formerly termed fluate of lime, is, in fact, a compound analogous to calcium chloride, containing the metal calcium combined with an element similar to chlorine, termed fluorine (from *fluo*, I flow, because of the use of fluor-spar as a flux in smelting operations). Even up to recent years the nature and constitution of the fluorine compounds have been discussed; and it is only within the last two or three decades that Gore's researches taken together with the preparation of organic fluorides have definitely proved the true analogy of the hydrogen compounds of fluorine and chlorine, while in 1891 Moissan succeeded in isolating fluorine, and thus solved one of the most difficult problems of modern chemistry. The reason why fluorine has for so long resisted the innumerable attempts which have been made to isolate it, will be easily understood from its properties.

88 Moissan obtained fluorine by the electrolysis of pure and perfectly anhydrous hydrofluoric acid in which some potassium hydrogen fluoride was dissolved in order to enable the liquid to conduct the electric current, which hydrofluoric acid by itself is incapable of doing. The latest form of apparatus employed by Moissan consists of a U-shaped tube of iridioplatinum with two small platinum side tubes attached, and possessing a capacity of about 160 c.c., in which a mixture of about 100 grams of anhydrous hydrofluoric acid and twenty grams of potassium hydrogen fluoride is placed. The construction of the vessel is seen in Fig. 31; the open ends are closed by stoppers (F) of fluor-spar, ground so as nearly to fit the tube and wrapped round by thin platinum foil. The electrodes of iridioplatinum (*t t*) pass through the stoppers, which are held in position by brass caps and screws (E), the joints being rendered air-tight by placing leaden washers at *p*, and coating all the surfaces with shellac. During the electrolysis, for which twenty-five Bunsen cells

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[1] *Ann. Chim. Phys.*, 1807, [1], **69**, 204.

arranged in series are required, the platinum U-tube filled with the mixture of hydrofluoric acid and potassium fluoride is placed in a glass cylinder as shown in Fig. 32, into which liquid methyl chloride is passed from the steel cylinder. This liquid at once boils, and the temperature is reduced to −23°, at which the electrolysis is carried on. A second glass cylinder surrounds that in which the methyl chloride is evaporating, and contains fragments of calcium chloride to dry the air and thus prevent the formation of hoar-frost on the inner cold cylinder.[1]

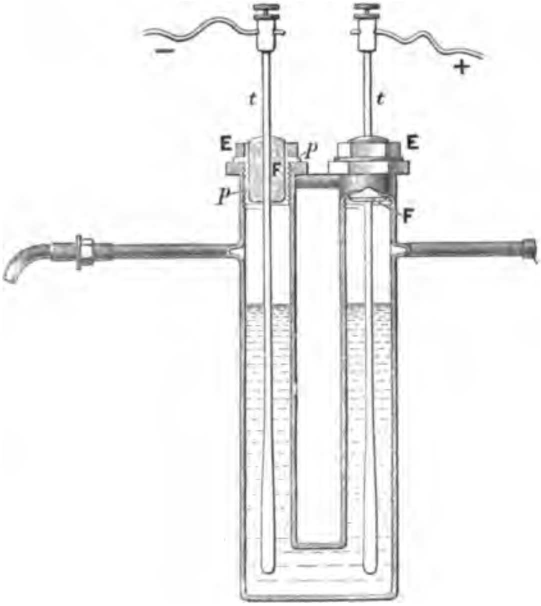

FIG. 31.

Pure hydrogen is evolved from the negative pole and is carried off by the platinum exit-tube to the left of the figure. Fluorine is evolved at the positive pole and passes from the U-tube to a spiral tube of platinum also placed in a glass cylinder containing rapidly evaporating methyl chloride, so that the temperature is kept at about −50°. This serves to retain hydrofluoric acid vapours which are carried over with the gaseous fluorine, whilst the latter passes on through two platinum tubes containing lumps of sodium fluoride, a salt which

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Ann. Chim. Phys., 1887, [6], **12**, 473; 1891, [6], **24**, 226.

absorbs the last traces of hydrofluoric acid. The decomposition is represented by the equations

$$(1)\ 2KF = 2K + F_2,$$
$$(2)\ 2K + 2HF = 2KF + H_2,$$

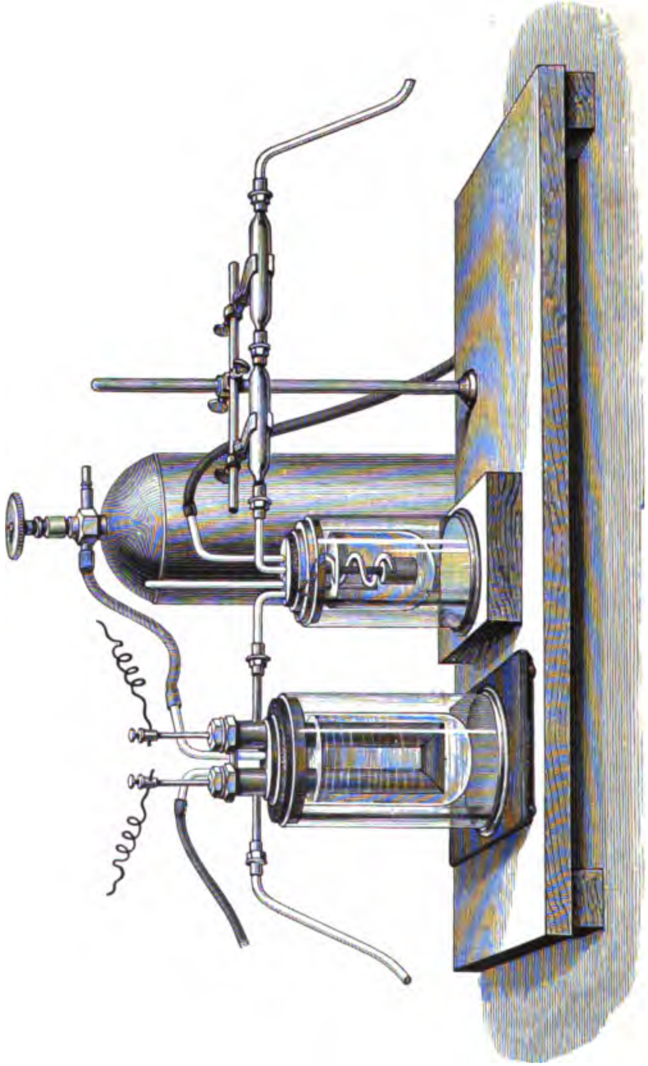

FIG. 32.

but the platinum electrode at which the fluorine is liberated is much corroded with formation of a certain quantity of a black powder consisting of platinum fluoride. The volume of fluorine obtained with this apparatus is from three to four litres per hour. Copper vessels may also be employed in place of platinum, but the electrodes must consist of the latter metal.[1]

In order to prove that the gas evolved by electrolysis is in reality fluorine and not a higher hydrogen compound of that element, Moissan attached to the fluorine delivery tube a weighed platinum tube containing iron wire, whilst to the negative delivery tube an arrangement for collecting and measuring the hydrogen was attached. On starting the electrolysis, and heating the platinum tube containing the iron wire, the whole of the fluorine was absorbed with formation of iron fluoride, whilst the hydrogen simultaneously evolved was collected and measured. As the mean of two experiments it was found that 79 c.c. of hydrogen weighing 0·00703 gram were obtained; this corresponds to 0·1335 of fluorine, whereas the mean increase of weight of the iron was 0·135 gram.

Fluorine is also formed in small quantity by heating certain double salts of cerium tetrafluoride and lead tetrafluoride. Thus potassium fluorplumbate, $3KF,HF,PbF_4$, when heated to 230—250° loses hydrofluoric acid, and on further heating gives off a gas containing free fluorine at temperatures below a red heat.[2]

89 *Properties of Fluorine.*—Fluorine is a light greenish-yellow gas, paler and more purely yellow in colour than chlorine, possessing a penetrating odour resembling that of hypochlorous acid. Moissan's earlier determinations of the sp. gr. of the gas at the ordinary temperature gave the number 1·26, which is decidedly less than that required by the formula, F_2 (1·316), and it therefore appeared not unlikely that some of the fluorine molecules at that temperature might consist of single atoms, a supposition which would partly account for the intense chemical activity of the gas. Later determinations by Moissan[3] have, however, shown that the sp. gr. is in reality 1·31, this number being the mean of four closely agreeing determinations; there can therefore be no considerable proportion of free atoms in the gas at the ordinary temperature. When cooled by liquid air boiling in a vacuum, it condenses to a clear yellow liquid, boiling at $-187°$ under atmospheric pressure, and having a sp. gr. of 1·14. It solidifies, when cooled by liquid hydrogen, to a pale yellow solid,

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[1] Moissan, *Compt. Rend.*, 1899, **128**, 1543.

[2] Brauner, *Journ. Chem. Soc.*, 1882, 68; 1894, 399.

[3] *Compt. Rend.*, 1904, **138**, 728.

which melts at −223°, and becomes perfectly white at −252°.[1] It does not fume in dry air, but does so in presence of moisture, hydrofluoric acid being formed and ozone set free, whilst the gas even in small quantity exerts a most irritating effect on the eyes and mucous membrane.

In order to observe the action of fluorine on gases a platinum tube (Fig. 33) is employed, closed at each end by transparent plates of fluorspar; the fluorine is passed into the observation tube by one of the small platinum side tubes and the other gas by the second, whilst the resultant of the action passes out by the platinum delivery tube. To examine the action of the gas on liquids or solids it suffices to place the substance to be examined in a test tube, and to allow the fluorine to pass into the latter from the electrolytic apparatus, the gas having no marked action on dry glass.

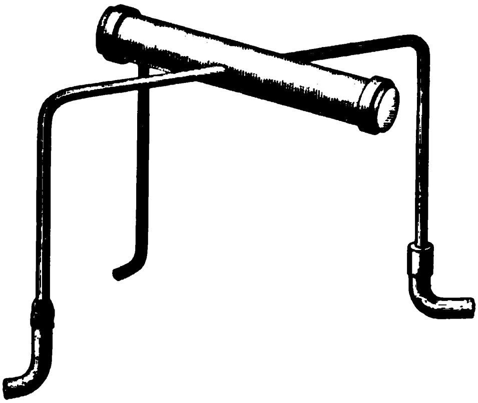

Fig. 33.

Fluorine is the most active element with which we are acquainted. It combines explosively with hydrogen in the dark; the direct combination may be shown more simply than with the above-mentioned apparatus by simply inverting a jar filled with hydrogen over the positive exit tube of the electrolytic apparatus. As soon as the fluorine comes in contact with the hydrogen a blue, red-bordered flame appears at the end of the platinum tube, hydrofluoric acid being formed which slowly attacks the glass jar. It decomposes water with the utmost

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[1] Moissan and Dewar, *Proc. Chem. Soc.*, 1897, 175; *Compt. Rend.*, 1903, **136**, 641.

avidity, uniting with the hydrogen to form hydrofluoric acid, and liberating ozone, and therefore in all experiments with the gas the presence of moisture must be excluded as completely as possible.

Fluorine at once liberates chlorine from potassium chloride and carbon tetrachloride at the ordinary temperature; sulphur and selenium quickly melt and take fire in the gas, and tellurium like the former elements also combines directly with formation of a fluoride. With iodine, bromine, phosphorus, arsenic and antimony it combines with incandescence; crystallised silicon, amorphous boron, and finely divided carbon such as lamp-black and charcoal, when thrown into fluorine take fire and burn with formation of fluorides. The alkali-metals and those of the alkaline earths ignite in the gas; lead is slowly transformed into the fluoride, and finely divided iron becomes red hot on exposure to the gas. Magnesium, aluminium, manganese, nickel and silver when slightly warmed burn brightly in fluorine; gold is not attacked at the ordinary temperature, but between 300° and 400° becomes covered with a yellow coating of gold fluoride, and platinum under similar conditions yields two fluorides, which like the gold compound readily decompose into the metal and fluorine at a dull red heat.

Fluorine retains its chemical activity largely unimpaired at the lowest temperatures yet attained. Thus if a tube of fluorine is immersed in liquid hydrogen and the tube broken after its temperature is in equilibrium with that of the liquid hydrogen ($-252°$), a violent explosion occurs with incandescence and complete destruction of the vessel containing the liquid hydrogen (Moissan and Dewar). Its combining power with most of the other elements appears to be but little diminished at its boiling point, but it does not liberate iodine from potassium iodide below this temperature, nor does it then combine with elementary iodine.

The atomic weight of fluorine has been determined by several chemists by converting either calcium fluoride, potassium fluoride, or sodium fluoride into the corresponding sulphate. The mean of fairly agreeing experiments gives the number 18·9. ($H = 1$.)

FLUORINE AND HYDROGEN.

HYDROFLUORIC ACID. HF = 19·9.

90 Anhydrous hydrofluoric acid, HF, is a volatile colourless liquid, best obtained, according to Fremy[1] and Gore,[2] by heating to redness in a platinum retort the double fluoride of hydrogen and potassium HF + KF, which has been previously fused. A description of the process employed for preparing pure hydrofluoric acid may give an idea of the difficulty and danger of chemical investigations on fluorine and fluorides, as well as of the precautions which must be taken.

(1) For this purpose about 200 grams of the fused salt were placed by Gore in a platinum bottle, or retort (*a*, Fig. 34). No vessels of glass, porcelain, or other substance containing silica can be used in the preparation of this acid, as the silica is at once attacked by hydrofluoric acid unless it is absolutely anhydrous, a volatile tetrafluoride of silicon and water being formed, thus:—

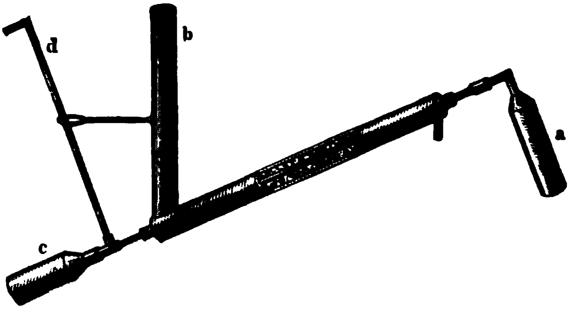

FIG. 34

$$4HF + SiO_2 = 2H_2O + SiF_4.$$

The platinum bottle was then gently heated so as to fuse the salt, and thus completely drive off any traces of water. The long platinum tube was then connected by means of a lute of fused sulphur to the neck of the bottle, the condenser surrounding this tube being filled with a freezing mixture poured

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[1] *Ann. Chim. Phys.*, 1856 [3], **47**, 5.

[2] *Phil. Trans.*, 1869, 173.

through the open tube *b*, whilst the platinum bottle *c*, immersed in a freezing mixture, was employed to receive the distillate. This bottle was provided with an exit-tube of platinum, upon the upper end of which a short angle tube *g* of platinum, turned downwards, was fixed to prevent condensed moisture from running down into the bottle. On gradually raising the temperature, the fused salt begins to decompose, hydrofluoric acid is given off as a gas, which condenses in the platinum tube and runs into the platinum bottle. Great care must be taken to have all the apparatus free from moisture, and the acid must be re-distilled in order to remove traces of saline matter which are apt to be carried over. According to Moissan, the acid thus obtained still contains traces of moisture, which can only be removed by subjecting the liquid to electrolysis, the water present being then decomposed by the fluorine evolved with formation of hydrofluoric acid and ozone.

The acid thus obtained is a highly dangerous substance, and requires the most extreme care in its manipulation, the inhalation of its vapour having produced fatal effects.[1] A drop on the skin gives rise to blisters and sores which only heal after a very long period. From its great volatility the anhydrous acid can only be safely preserved in platinum bottles having a flanged mouth, a platinum plate coated with paraffin being tightly secured to the flanged mouth by clamp screws. The acid must be kept in a cool place not above a temperature of 15°, otherwise it is very likely to burst the bottle; and a freezing mixture should always be at hand when experimenting with it (Gore).

Anhydrous hydrofluoric acid can also be obtained by acting on dry silver fluoride with hydrogen.

(2) If the hydrofluoric acid is not required to be perfectly anhydrous a much easier process than the foregoing can be adopted. This consists in the decomposition of fluor-spar by strong sulphuric acid, when hydrofluoric acid and calcium sulphate are formed, thus:—

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

For this preparation vessels of platinum, or, on the large scale, vessels of lead, can be employed. On heating the mixture, the nearly anhydrous acid which distils over can be condensed either

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[1] Professor Nicklès, of Nancy, died in 1869 from accidentally breathing the vapour of this acid whilst endeavouring to isolate fluorine.

by passing through a tube placed in a freezing mixture, or into a small quantity of water contained in a platinum dish if a dilute acid be needed. The dilute acid may be preserved in gutta-percha bottles, but this substance is at once acted upon by the anhydrous acid.

One form of platinum apparatus used for preparing the gas is shown in Fig. 35. The U-tube is placed in a freezing mixture when the gas has to be condensed. If an aqueous solution of the acid is needed, the arrangement shown in Fig. 36 may be employed. It consists of a leaden retort, *a*, on to which a leaden head, *c*, can be cemented at *bb′*. The neck of the retort fits into a leaden receiver at *e*, in which is placed a platinum basin containing water. The acid vapours are absorbed by the water, and thus a solution of the acid is obtained free from lead, which would not be the case if the water had been simply placed in the leaden vessel. The tube *g* serves to allow the escape of air and of excess of hydrofluoric acid gas.

FIGS. 35, 36.

91 *Properties.*—The specific gravity of liquid anhydrous hydrofluoric acid at 15° is 0·9879 (Gore), or it is a little lighter than water. It boils at 19°·4, and solidifies at −102°·5, melting again at −92°·3. If it is perfectly dry it does not act on glass; the slightest trace of moisture, however, renders it capable of doing so. The acid scarcely acts upon the non-metals or on the noble metals, and the other metals do not decompose it below 20°. Potassium and sodium dissolve in it as in water with evolution of hydrogen and formation of a fluoride; it decomposes the carbonates with effervescence and with formation of fluorides.

The composition by volume of the anhydrous acid was ascertained by Gore by measuring the volume of hydrogen needed to combine with the fluorine contained in a given weight of silver fluoride. From this and other experiments he arrived at the conclusion that one volume of hydrogen necessarily yields two volumes of hydrofluoric acid gas, and that this contains for every one part by weight of hydrogen 19·1 parts by weight of fluorine.

Thorpe and Hambly[1] have shown that the vapour density of hydrofluoric acid varies rapidly with variation of temperature and pressure. The following table gives the results of their experiments at temperatures between 26°·4 and 88°·1 :—

Temp.	Pressure of Vapour in mm.	V.D. air 1.	Molecular weight.
26°·4	745	1·773	51·18
27°·8	746	1·712	49·42
29°·2	750	1·578	45·54
32°·0	743	1·377	39·74
33°·1	750	1·321	38·12
33°·8	758	1·270	36·66
36°·3	739	1·115	32·20
38°·7	751	1·021	29·46
39°·2	743	1·002	28·94
42°·8	741	0·910	26·26
47°·3	745	0·823	23·76
57°·5	750	0·737	21·28
69°·4	746	0·726	20·96
88°·1	741	0·713	20·58

These numbers show that the process of dissociation of the vapour of hydrogen fluoride is quite continuous, and that therefore there is no evidence of the existence of molecules H_2F_2, as was formerly supposed. It was also found that the vapour density is lowered by diminishing the pressure of the gas at a constant temperature of about 32°.

Hydrofluoric acid is very soluble in water, the specific gravity of the solution rising to 1·25. The concentrated aqueous acid becomes weaker on boiling until at 120° it attains a constant composition of from 36 to 38 per cent. of the anhydrous acid, but it does not thus form a definite hydrate ; when allowed to evaporate over caustic lime in the air, the aqueous acid attains a constant composition, containing 32·6 per cent. of the anhydrous acid.[2]

92 *Qualitative Detection of Fluorine.*—In order to test for the

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[1] *Journ. Chem. Soc.*, 1889, 163.

[2] Roscoe, *Journ. Chem. Soc.*, 1861, 162.

presence of hydrofluoric acid, its power of etching on glass is made use of. For this purpose a small piece of glass is covered with a thin and even film of melted bees'-wax, and, after cooling, some lines or marks are made by removing the wax by a sharp but not a hard point. The dry substance to be tested is placed in a platinum crucible or small leaden cup, and covered with strong sulphuric acid, the crucible being gently warmed; after the lamp has been removed, the slip of covered glass is placed on the crucible and allowed to remain for ten minutes. The wax can then be re-melted and wiped off with blotting paper, when the etching, indicating the presence of fluorine, will be seen. In performing this experiment it is well to remember, on the one hand, that if the quantity of fluorine present be very small, the etching may not at once be visible but may become so by breathing on the surface of the glass, whilst, on the other hand, if the point employed to remove the wax be a hard one, a mark or scratch may sometimes thus be seen on the glass when no fluorine is present. A more delicate test is to heat the substance suspected to contain the element with sand and sulphuric acid, and to place a moistened glass rod in the gas evolved, a film of silica being produced if fluorine is present.

93 *Fluorides.*—The compounds of fluorine with the metals are best formed by acting on the metal or on its oxide, hydrate, or carbonate, with hydrofluoric acid. The fluorides of the alkalis and of silver as well as those of most heavy metals dissolve in water; those of the alkaline earths are insoluble; and those of the earths, with the exception of fluoride of yttrium, are soluble in water. Most of the fluorides unite with hydrofluoric acid to form crystalline compounds, which are termed the acid fluorides. They also have a remarkable facility of union among themselves giving rise to double salts, which frequently crystallise well. They are all decomposed by treatment with sulphuric acid, yielding hydrofluoric acid and a sulphate, whilst some, as the silver salt, even undergo the same decomposition in presence of hydrogen alone.

The divisions on the glass of eudiometers and thermometers are etched by hydrofluoric acid, which is evolved from a mixture of fluor-spar and strong sulphuric acid in a long leaden trough, over which are placed the glass tubes covered with wax, and having the divisions marked upon them by scratching off the wax. The etching is best effected in the cold, and with anhydrous hydrofluoric acid; the tube must in this case be exposed for some hours to the action of the gas, and the trough covered with several folds of thick paper.

CHLORINE. Cl. = 35·18 (H = 1).
= 35·45 (O = 16).

94 Chlorine gas was first obtained and its properties first examined by Scheele[1] in 1774; he prepared it by the action of hydrochloric acid on manganese ore, and termed it "dephlogisticated marine acid gas." Berthollet, in 1785,[2] showed that, according to the then prevailing antiphlogistic theory, chlorine could be regarded as a compound of hydrochloric acid gas with oxygen; and this view of its constitution was held until the year 1810, when Davy[3] satisfactorily proved the elementary nature of the gas and gave it the name which it now bears. (χλωρός, greenish-yellow), Gay-Lussac and Thénard[4] having in the year 1809 discussed and rejected the suggestion that it might be considered to be a simple body.

Chlorine does not occur in the free state in nature, but is found in large quantities combined with the alkali metals, forming the chlorides of sodium, potassium, and magnesium, which constitute the largest proportion of the solid components of sea-water. Sodium chloride, $NaCl$, also occurs as rock-salt, in large deposits in the tertiary formation in various localities, whilst the chloride of potassium, although occurring less frequently, is found in certain localities, as in the salt beds of Stassfurt, in Germany, both in the pure state, as sylvine KCl, and in combination with chloride of magnesium and water, as carnallite $KCl, MgCl_2 + 6H_2O$. The chlorides and oxychlorides of several other metals also occur in nature, although in small quantities; thus we have lead oxychloride $PbCl_2PbO$, known as matlockite; ferric chloride $FeCl_3$, found in the craters of volcanoes; silver chloride, or horn silver, $AgCl$; copper oxychloride, or atacamite, $Cu_2Cl(OH)_3$, and many others.

The chlorides of the alkalis occur in the bodies of plants and animals, and play an essential part in the economy of the

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[1] *Opusc.*, Tome 1, 247.

[2] *Mém. de l'Acad. des Sciences*, Paris, 1785, p. 276.

[3] *Phil. Trans.*, 1811, pp. 1 and 32; *Bakerian Lecture for* 1810, read Nov. 10th, 1810.

[4] *Mémoires d'Arcueil*, Tome 2, 357.

animal and vegetable worlds. Chlorine likewise occurs combined with hydrogen, forming hydrochloric acid, a substance which is found in nature in small quantities in certain volcanic gases.

95 *Preparation.*—(1) Pure chlorine gas is best prepared by the electrolysis of pure fused silver chloride, using carbon electrodes, the salt being thus split up into its elements. Pure chlorine is evolved from the positive pole, whilst metallic silver separates at the negative pole.[1]

(2) Chlorine is usually prepared when a high degree of purity is not required, by the action of black oxide of manganese (manganese dioxide) on strong hydrochloric acid, thus:—

$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O.$$

When these two substances are brought together, a dark greenish-brown solution is first obtained, and this on heating evolves chlorine gas, whilst manganous chloride $MnCl_2$ is formed. There is little doubt that the dark-coloured solution contains a higher unstable manganese chloride, probably $MnCl_3$ or $MnCl_4$, which has not yet been isolated, and which on heating decomposes into chlorine and manganous chloride.

In preparing the gas by this method the oxide of manganese should be in the form of small lumps free from powder, and the hydrochloric acid poured on so as to about cover the solid; on gently warming, the gas is copiously evolved.

(3) It is often more convenient for laboratory uses to liberate the hydrochloric acid in the same vessel in which it is acted upon by the manganese dioxide, and for this purpose to place a mixture of one part of the latter substance and one part of common salt in a large flask (Fig. 37) containing a cold mixture of two parts of strong sulphuric acid and two of water; on very slightly warming the mixture, a regular evolution of gas takes place. The change which here occurs was formerly supposed to be represented by the equation:—

$$2NaCl + 3H_2SO_4 + MnO_2 = Cl_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$$

according to which the whole of the chlorine is evolved in the free state. Klason[2] has shown, however, that this is not the case, the correct equation being as follows:—

$$\begin{gathered}4NaCl + MnO_2 + 3H_2SO_4 = \\ Cl_2 + 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O.\end{gathered}$$

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[1] Shenstone, *Journ. Chem. Soc.*, 1897, 479; Mellor and Russell, *Journ. Chem. Soc.*, 1902, 1274.

[2] *Ber.*, 1890, **23**, 334.

In order to purify and dry the gas prepared by either of the above methods, it is necessary to pass it, first through a wash bottle (*b*, Fig. 38) containing water, to free it from any hydrochloric acid gas which may be carried over, then through a second wash bottle (*a*) containing strong sulphuric acid, to free it from the larger quantity of the aqueous vapour which it takes up from the water, and lastly through a long inclined tube (*c*) containing pieces of pumice-stone moistened with strong and boiled sulphuric acid. The tube (*d*) which dips under water serves as a safety-tube in case the evolution of gas becomes too rapid, when the excess of gas can thus escape. In order to expel the air which fills the apparatus, the evolution of the chlorine must be allowed to go on until the gas is almost entirely absorbed by a solution of caustic soda. As the crude black oxide of manganese frequently contains calcium carbonate, the presence of which will cause the admixture of small quantities of carbon dioxide, CO_2, with the chlorine, it is advisable to moisten the ore before using it with warm dilute nitric acid, which will dissolve out the calcium carbonate, leaving the manganese dioxide unacted upon; after well washing, the latter may be used without danger of introducing this impurity.

FIG. 37.

(4) Besides manganese dioxide, many other oxidising agents may be employed for liberating the chlorine from hydrochloric

acid, as for example potassium bichromate or permanganate, both of which yield a fairly pure product when heated with the acid, potassium chloride together with chromic or manganous chloride being simultaneously produced :

$$K_2Cr_2O_7 + 14HCl = 3Cl_2 + 2CrCl_3 + 2KCl + 7H_2O.$$
$$2KMnO_4 + 16HCl = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O.$$

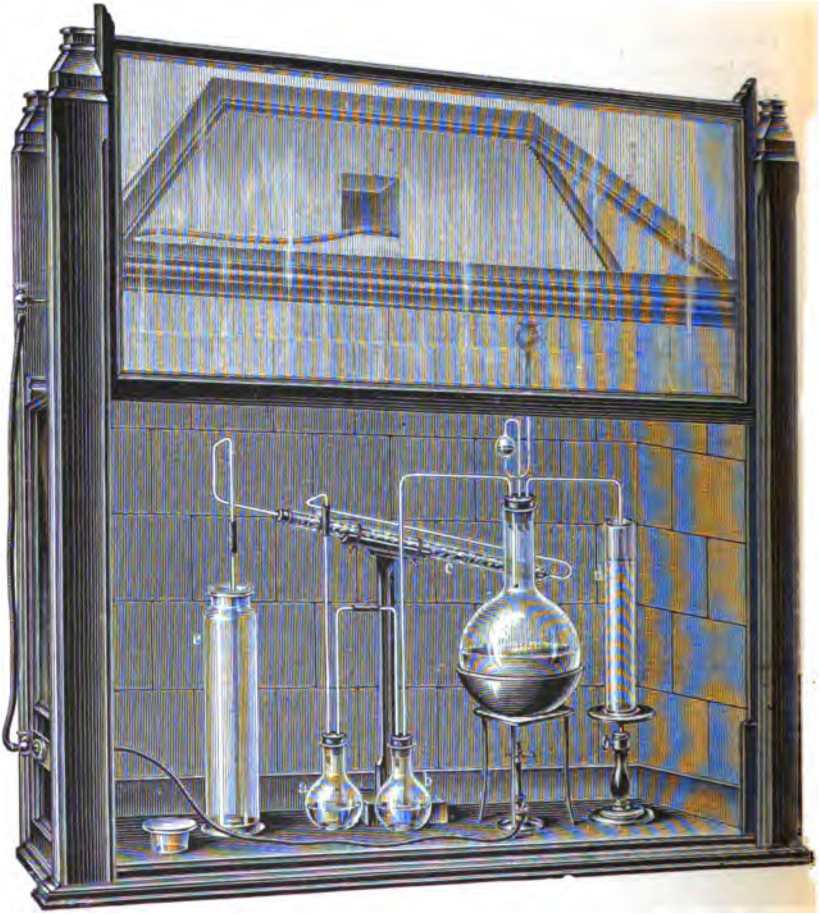

FIG. 38.

(5) Chlorine gas is also evolved when an acid is added to an alkali hypochlorite or to bleaching powder, the acid first liberating hypochlorous acid, which is decomposed by the excess of hydrochloric acid with formation of chlorine and water (see

Hypochlorous Acid). To prepare it from bleaching powder, the latter is made coherent by mixing it with plaster of Paris or by compressing it to form a solid cake, which is afterwards broken into lumps of suitable size.[1] As the evolution of the gas takes place at the ordinary temperature the Kipp's apparatus shown later under sulphuretted hydrogen may be employed, by which a current of the gas can be obtained as required.

96 *Manufacture of Chlorine on the Large Scale.*—For manufacturing purposes method (2) is largely employed. The black oxide of manganese and hydrochloric acid are placed in large square tanks, made of Yorkshire flags clamped together by iron rods, and the joints made tight by a rope of vulcanised caoutchouc. On heating the mixture by a steam-pipe the chlorine gas is evolved. For a description of the details of this mode of manufacture, see Bleaching Powder. (Vol. II. [1897], p. 428.)

Another method of manufacture consists in passing a mixture of air and hydrochloric acid over heated bricks, a portion of the hydrogen of the hydrochloric acid being oxidised with formation of water and chlorine gas (Oxland, 1847). If the mixture of gases be allowed to pass over a heated surface impregnated with certain metallic salts, especially sulphate of copper, the oxidation of the hydrogen of the hydrochloric acid goes on to a greater extent, and by the absorption of the unaltered hydrochloric acid a mixture of chlorine and nitrogen gases can be obtained. This process, patented by the late Mr. Henry Deacon, of Widnes, is used on a large scale for the economic production of chlorine and bleaching powder. The singular and but imperfectly understood decomposition which takes place may be shown on a small scale by the following arrangement:—

The hydrochloric acid gas is evolved from common salt and sulphuric acid in the large flask *a*, Fig. 39; this gas passes into the tube *b*, in which are placed pieces of tobacco-pipe moistened with a saturated solution of copper sulphate, the tube being exposed to a gentle heat. As the hydrochloric acid enters the tube containing the sulphate of copper it mixes with atmospheric air, which is driven in by the tube *c*, from the gasholder. On passing over the heated copper sulphate, the hydrochloric acid and the oxygen of the air act upon one another, water and chlorine gas being formed according to the equation

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

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[1] Winkler, *Ber.*, 1887, **20**, 184; Thiele, *Annalen*, 1889, **253**, 239.

FIG. 39.

The part played by the copper sulphate is unknown, but it continues active for a considerable length of time. The mixture of chlorine, nitrogen, steam, and any undecomposed hydrochloric acid passes by a bent tube into a bottle, *e*, containing water, by which the last-named substance is arrested, together with a portion of the steam which is condensed; the mixed gases, still containing some aqueous vapour, are then passed through a tube, *d*, containing calcium chloride, by which the gases are dried, after which the chlorine mixed with the nitrogen may be collected by displacement in a cylinder.

A large number of processes have been patented for the manufacture of chlorine from the solution of calcium or magnesium chloride produced in the manufacture of soda from common salt by the ammonia-soda process. These have, however, for the most part been insufficiently economical to compete with the processes already described. One of the most successful is the Weldon-Pechiney process, in which the ammonium chloride mother liquors are heated with magnesia to recover the ammonia, and the resulting magnesium chloride solution concentrated and mixed with sufficient magnesia to form the oxychloride Mg_2OCl_2. The latter is heated first to 250—300° in air, whereby the water present, together with at most 8 per cent. of the total chlorine in the form of hydrochloric acid, is evolved; the temperature is then gradually raised to 1000°, the mixture of air, chlorine, and hydrochloric acid being continuously drawn off, the latter removed by washing with water, and the chlorine then converted into bleaching powder or potassium chlorate.[1] (See also p. 177.)

97 *Electrolytic Manufacture of Chlorine.*—Beside the methods of manufacturing chlorine already described, which depend on the oxidation of the hydrogen of hydrochloric acid, or on the decomposition of certain chlorides by moisture in the presence of oxygen, there are other quite different methods in which chlorides are decomposed by passage of an electric current, so that chlorine gas is evolved on the one electrode and simultaneously a metal is set free on the other electrode, this latter remaining in the metallic condition or being acted upon by the water present, forming a metallic hydroxide and hydrogen. Chlorine was first manufactured electrolytically about 1890, and with the improvements since effected in methods and apparatus, the amount so manufactured has increased rapidly.

The electrolysis of hydrochloric acid, which has long been known in the laboratory, cannot be carried out on a

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[1] See Dewar, *Journ. Soc. Chem. Ind.*, 1887, **6**, 775; Kingsett, *ibid.*, 1888, **7**, 286.

manufacturing scale, but the aqueous solutions of the chlorides of potassium, sodium, or zinc—especially the two former—are electrolysed on a very large scale, producing many thousands of tons of chlorine yearly. Several attempts have been made, with partial success, to electrolyse fused chlorides, but practical difficulties have hitherto prevented the development of these processes.

The alkali chloride solutions are electrolysed with anodes of carbon or sometimes of platinum, and with cathodes of either (1) iron or other solid conductor on which the alkali metal, theoretically deposited, at once decomposes the water present, forming hydrogen and caustic alkali solution, or (2) mercury which at once alloys with the alkali metal as fast as it is deposited. The chlorine evolved at the anode rises through the solution, and is led away from the upper part of the apparatus by suitable pipes, the gas obtained with certain forms of apparatus having a high degree of purity. The advantages of the electrolytic preparation of chlorine from sodium chloride are that the raw product is far cheaper than hydrochloric acid, and that caustic soda is obtained as a bye product; a similar advantage to this last, holds when potassium chloride is electrolysed for chlorine. As the essential points in the construction of apparatus are concerned with the method of removing the caustic alkalis from the sphere of the electrolysis, the apparatus will be described later under Caustic Soda (Vol. II. [1897], p. 215).

The electrolysis of zinc chloride solution as far as the evolution of the chlorine is concerned is quite similar to the electrolysis of the alkali chlorides, but the zinc is deposited in a permanently metallic condition upon the cathodes. The zinc chloride solution is prepared from the waste calcium chloride liquors of the ammonia-soda process by heating them under pressure with finely powdered native zinc carbonate, when a partial reaction proceeds according to the equation

$$CaCl_2 + ZnCO_3 = ZnCl_2 + CaCO_3.$$

Zinc oxide obtained by roasting the native sulphide may be used in place of the more expensive carbonate, but the oxide has then to be converted into carbonate by forcing in carbonic acid gas during the heating, and the zinc carbonate finally reacts exactly as in the preceding equation. In either case the precipitate of calcium carbonate is filtered off from the solution of zinc chloride, and the clear solution electrolysed.[1] Up to 1902 about 1,700 tons of chlorine had been so prepared at Messrs. Brunner, Mond and Co.'s works at Winnington, and the daily production was then three tons. This process affords another method of utilising the chlorine in the waste liquors from the ammonia-soda process (p. 175).

98 *Properties.*—Chlorine at the ordinary atmospheric temperature and pressure is a transparent gas of a greenish-yellow colour, possessing a most disagreeable and powerfully suffocating smell, which, when the gas is present in small quantities only, resembles that of seaweed, but when it is present in large quantities acts as a violent irritant, producing coughing, inflammation of the mucous membranes of the throat and nose, and, when inhaled in the pure state, even death.

The specific gravity of chlorine at 0° is 2·491 (air = 1),[2] which is rather higher than is demanded by the molecular formula Cl_2. The density, however, gradually decreases with increasing temperature, until at 200° it reaches a constant value of 2·45 compared with air at the same temperature, or of 35·26 compared with hydrogen. At this temperature, therefore, its molecular formula is Cl_2. This density is maintained up to about 1,200°, above which it again decreases, and at 1,400° is only 2·02, the diatomic molecules Cl_2 being partly split up into monatomic molecules at this temperature.[3]

When subjected to pressure at the ordinary temperature, or to a temperature below −34° under atmospheric pressure, chlorine condenses to a liquid which solidifies at −102°,[4] boils at −33·6°,[5] and at 0° has a sp. gr. of 1·4405 and a vapour pressure of 3·66 atmospheres. The critical temperature of the liquid is 146°.[6]

Liquid chlorine has a yellow colour, with a tinge of orange in thick layers, is not miscible with water, does not conduct electricity, and has a refractive index lower than that of water: it is now prepared commercially, and brought into the market in cylinders containing 5 kilos. of the liquid.

Chlorine gas dissolves in about half its volume of cold water, and as the gas instantly attacks mercury, it must either be collected in the pneumatic trough over hot water, or by displacing

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[1] C. Höpfner, *Journ. Soc. Chem. Ind.*, 1895, 581 ; 1896, 198.
[2] Leduc, *Compt. Rend.*, 1897, **125**, 571.
[3] Langer and Meyer, *Pyrochem. Untersuch.*, p. 46 (Vieweg, 1885).
[4] Olszewski, *Monatsh.*, 1884, **5**, 127.
[5] Faraday, *Phil. Trans.*, 1823, 160.
[6] Knietsch, *Annalen*, 1889, **253**, 100.

the air from a dry cylinder, as shown in Fig. 39, care being taken that the excess of chlorine is allowed to escape into a draught cupboard, as represented in the drawing.

99 *Combustions in Chlorine.*—Chlorine is not inflammable, and does not directly combine with oxygen; it unites, however, with great energy with hydrogen, forming hydrochloric acid, HCl, and to this property it owes its peculiar and valuable bleaching power. It also combines with many metals, giving rise to a class of compounds termed the metallic *chlorides.*

In each case of combination with chlorine a definite quantity of heat is given out, whilst sometimes light is also emitted, so that the essential phenomena of combustion are observed. Thus if we plunge a jet from which a flame of hydrogen burns into a cylinder of chlorine gas (Fig. 40), the hydrogen continues to burn, but instead of water being produced, hydrochloric acid is formed by the combustion. In like manner, if we bring a light to the mouth (held downwards) of a cylinder of hydrogen and then bring this over a jet from which chlorine gas is issuing (Fig. 41), a flame of chlorine burning in hydrogen will be seen.

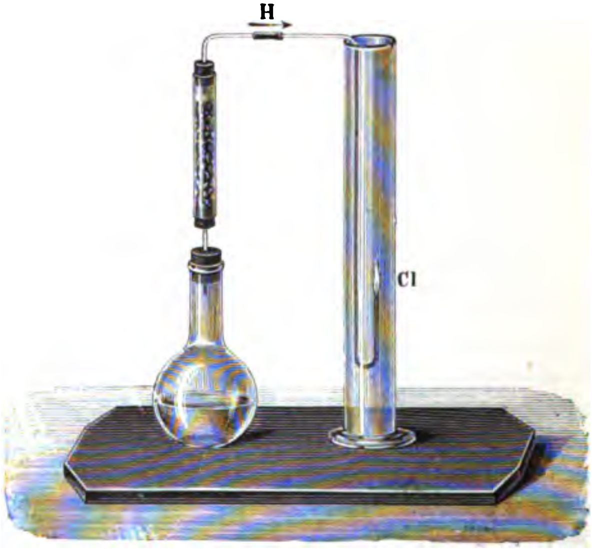

FIG. 40.

If two equal sized cylinders, filled, one with chlorine and the other with hydrogen, are brought mouth to mouth, the two glass plates closing them withdrawn, and the gases allowed to mix, and if then a flame is brought near the mouths of the cylinders, the mixed gases combine with a peculiar noise, and dense fumes of hydrochloric acid gas are seen. This experiment must, however, be made in a room partially darkened, or performed by gas- or candle-light, as the two gases combine with explosion in sunlight or strong daylight.

The following experiments are cited as showing the power with which chlorine unites with hydrogen, even when the latter is combined with some other element.

Fig. 41.

Fig. 42.

(1.) If two volumes of chlorine be mixed with one volume of olefiant gas, C_2H_4, and a light quickly applied to the mixture, the chlorine immediately combines with the hydrogen of the latter to form hydrochloric acid, HCl, while the carbon is set free in the form of a black smoke, thus:—

$$C_2H_4 + 2Cl_2 = 4HCl + 2C.$$

(2.) If a piece of filter-paper be dipped in oil of turpentine,

$C_{10}H_{16}$, and plunged into a jar of chlorine gas, the paper bursts into flame; the chlorine combining with the hydrogen of the turpentine, while the carbon is deposited.

(3.) When sulphuretted hydrogen gas, H_2S, is passed into chlorine water, hydrochloric acid is formed by the union of the hydrogen of the former with the chlorine of the latter, and the sulphur is set free in the form of a light yellow precipitate.

(4.) When a lighted taper is plunged into a jar of chlorine, it continues to burn with a dull red light, and dense fumes as well as a cloud of black smoke are emitted, arising from the combination of the hydrogen of the wax with the chlorine, and the liberation of the carbon.

In order to exhibit the combination of certain elements with chlorine, whereby heat and light are evolved, the following experiments may be made:—

(1.) Place some leaves of Dutch metal (copper in thin leaves) in a flask provided with a stopcock (Fig. 42) and exhaust the flask with the air—or water—pump; attach the outer end of the stopcock to the neck of another flask containing moist chlorine gas. On opening the stopcock the chlorine will rush into the vacuous flask, and the copper leaf will take fire, dense yellow fumes of copper chloride being formed. (2.) Finely powdered metallic antimony thrown into a jar of chlorine gives rise to a shower of brilliant sparks, chloride of antimony being produced. If the jar be placed on the table over a powerful down-draught, all risk of escaping fumes will be avoided. (3.) A small piece of phosphorus placed in a deflagrating spoon and plunged into a jar of chlorine first melts, and, after a few minutes, bursts into flame with formation of the chlorides of phosphorus. (4.) Metallic sodium melted in a spoon also takes fire on immersion in the moist gas, burning brightly, with the production of common salt—sodium chloride; but it is a singular fact, first observed by Wanklyn,[1] that sodium may be melted in dry chlorine without any combination occurring, the surface of the molten metal remaining bright and lustrous. Cowper[2] has shown that other metals are also not attacked by dry chlorine.

100 *Action of Light on Chlorine.*—In 1843, Draper[3] found that chlorine which has been exposed to light combines more readily with hydrogen than that which has been kept in the dark.

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[1] *Journ. Chem. Soc.*, 1883, 153.

[2] *Chem. News*, 1869, **20**, 291.

[3] *Phil. Mag.*, 1845 [3], **27**, 327; 1857 [5], **14**, 161.

Bunsen and Roscoe[1] were unable to confirm this difference between "insolated" and "uninsolated" chlorine, but recently Bevan[2] and Burgess and Chapman,[3] have shown that with moist chlorine such a difference does exist; this increased activity is, however, lost when the gas is bubbled through water, as was the case in Bunsen and Roscoe's experiments. There does not seem any reason to assume, as has sometimes been done, that a different allotropic modification of chlorine is formed by the action of light, but rather that under the influence of the latter a reaction takes place between the chlorine and the moisture present, with formation of some substance, the nature of which is as yet unknown, but which facilitates the combination of the chlorine and hydrogen (see also p. 191).

A somewhat similar observation was made in 1870 by Budde,[4] who found that when chlorine is exposed to light-rays of high refrangibility it increases in volume; the result is the same when all heat-rays are filtered out by interposing a screen of water between the source of light and the chlorine, so that the expansion cannot be due to a direct heating effect of the rays. These results have been confirmed by Richardson,[5] Recklinghausen,[6] and Mellor[7] so far as moist chlorine is concerned, but the effect is not shown if the chlorine has previously been well dried.

Budde suggested as a possible explanation of the phenomenon that some of the chlorine molecules Cl_2 are dissociated into single atoms, but Mellor has shown that this supposition is untenable, as the increase of volume observed exactly corresponds with the increase of temperature which takes place. The rise in temperature is, therefore, probably due to some chemical reaction between the chlorine and moisture, brought about by the action of light.

Richardson has availed himself of this property of chlorine to construct a continuous recording actinometer. The apparatus consists of two bulbs connected by a narrow tube, one of which is filled with dry air and the other with chlorine, sulphuric acid being employed to separate the two gases. The bulbs are fixed on the beam of a balance in such a manner that the flow of acid from one arm to the other produces a movement of the

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[1] *Phil. Trans.*, 1857, ii. 378.
[2] *Phil. Trans.*, 1903, **202**, 71.
[3] *Proc. Chem. Soc.*, 1904, 52.
[4] *Phil. Mag.*, 1871 [5], **42**, 290.
[5] *Phil. Mag.*, 1891 [5], **32**, 277.
[6] *Zeit. physikal. Chem.*, 1894, **14**, 494.
[7] *Journ. Chem. Soc.*, 1902, 1284.

beam, which is communicated by means of a lever to a pen and is recorded on a rotating drum. By means of an ingenious compensating arrangement the expansion caused by the heat-rays is eliminated.[1]

101 *Bleaching Power of Chlorine.*—The characteristic bleaching action which chlorine exerts upon organic colouring matters, and which has become of such enormous importance in the cotton and paper trades, depends upon its power of combining with hydrogen. This bleaching action takes place only in presence of water, the colouring matter being oxidised and destroyed by the liberated oxygen of the water, whilst the hydrogen and chlorine combine together.

That dry chlorine does not act upon colouring matters may be readily shown by immersing a piece of litmus paper, or, better still, a small piece of turkey-red cloth, previously well dried, in a jar of dry chlorine, when the colour will remain for hours unaltered, whereas the addition of a small quantity of water causes its immediate disappearance.

Chlorine cannot as a rule destroy mineral colours, nor can it bleach black tints produced by carbon; this is well shown by rendering illegible the ordinary print (printer's ink is made with lamp-black or carbon) on a piece of card or paper, by covering the whole with common writing-ink (which generally consists of the iron salts of organic acids). On immersing the blackened card in moist chlorine gas, or in a solution of chlorine water, the printed letters will gradually make their appearance.

Chlorine also possesses powerful *disinfecting* properties, and the gas is largely used for the destruction of bad odours and of the poisonous germs of infectious disease floating either in the air or in water. It is probable that this valuable property also depends upon the oxidation, and consequently the destruction, of these bodies.

102 *Chlorine and Water. Hydrate of Chlorine.*—When chlorine gas is passed into water a few degrees above the freezing-point, a solid crystalline compound of the gas and water, termed chlorine hydrate, is formed. By quickly pressing the crystals between blotting-paper, they may be freed from adhering water and analysed. Faraday found that they contained 27·70 per cent. of chlorine, showing that they are composed of one atom of chlorine to five molecules of water, the hydrate having, therefore, the composition Cl_2+10H_2O.

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[1] *Phil. Mag.*, 1891 [5], **32**, 283.

According to Bakhuis Roozeboom they have the composition $Cl_2 + 8H_2O$,[1] whilst de Forcrand[2] gives the formula $Cl_2 + 7H_2O$. This hydrate forms beautiful, apparently regular octohedra, and decomposes readily, the temperature of decomposition being 9°·6 in open and 28°·7 in closed vessels; in the latter case it forms two layers, one of liquid chlorine, and the other of the aqueous solution of the gas. Liquid chlorine was first obtained in this manner by Faraday, the hydrate being warmed in the bent sealed tube shown in Fig. 43. When the other end is placed in a freezing mixture, the liquid chlorine distils over, leaving the less volatile chlorine water behind.

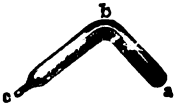

Fig. 43.

Fig. 44.

Aqueous Solution of Chlorine possesses a greenish-yellow colour and smells strongly of the gas. Chlorine is most soluble

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[1] *Rec. Trav. Chim.*, 1885, **3**, 59.

[2] *Compt. Rend.*, 1902, **134**, 991.

in water at 10°, as below this temperature the formation of the hydrate commences, and as the temperature increases above 10° the solubility diminishes, until at 100° no gas dissolves. It is prepared by passing washed chlorine gas through water as shown in Fig. 44, chlorine being evolved in the flask A, and the solution of the gas obtained in the bottles C, D, and E.

If we wish to absorb in water the whole of a small quantity of chlorine gas evolved in a given reaction, the apparatus represented in Fig. 45 may be used. Chlorine is led by a gas delivery-tube into an inverted retort having a wide neck and filled with water; the gas displaces some of the water, collects in the upper portion of the retort, and may there be absorbed and its quantity estimated.

FIG. 45.

The absorption coefficient of chlorine in water between 10° and 41°·5 is given by the equation

$$C = 3{\cdot}0361 - 0{\cdot}046196t + 0{\cdot}0001107t^2$$

from which the following values are obtained.

One volume of water absorbs the following volumes of chlorine gas calculated at 0° and 760 mm.[1]

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[1] Schönfeld, *Annalen*, 1855, **93**, 26; 1855, **96**, 8.

Temperatures Centigrade.	Coefficient.	Difference.	Temperatures Centigrade.	Coefficient.	Difference.
10	2·5852		26	1·9099	0·0405
11	2·5413	0·0439	27	1·8695	0·0404
12	2·4977	0·0436	28	1·8295	0·0400
13	2·4543	0·0434	29	1·7895	0·0400
14	2·4111	0·0432	30	1·7499	0·0396
15	2·3681	0·0430	31	1·7104	0·0395
16	2·3253	0·0428	32	1·6712	0·0392
17	2·2828	0·0425	33	1·6322	0·0390
18	2·2405	0·0423	34	1·5934	0·0388
19	2·1984	0·0421	35	1·5550	0·0384
20	2·1565	0·0419	36	1·5166	0·0384
21	2·1148	0·0417	37	1·4785	0·0381
22	2·0734	0·0414	38	1·4406	0·0379
23	2·0322	0·0412	39	1·4029	0·0377
24	1·9912	0·0410	40	1·3655	0·0374
25	1·9504	0·0408			

From a study of the electrical conductivity of chlorine water Jakowkin[1] has shown that this does not consist simply of a solution of chlorine in water, but that the former is partially converted into hydrochloric and hypochlorous acids, the change being a reversible one as represented by the equation

$$Cl_2,aq. + H_2O \rightleftarrows (HCl + HClO)aq.$$

This conclusion accounts for the result observed by Roscoe[2] that chlorine, when mixed with another gas, such as hydrogen or carbon dioxide, is absorbed by water at temperatures between 11° and 38° in greater quantities than that calculated from Dalton and Henry's law of partial pressures. It has further been shown by Richardson[3] that when chlorine water is distilled, hypochlorous acid continuously passes over together with free chlorine, leaving hydrochloric acid in the residue; but that if the distillation be conducted so that the condensed products flow back into the flask, the chlorine water is practically stable at the boiling-point.

Saturated chlorine water gives off chlorine freely on exposure to the air, and bleaches organic colouring matters. When

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[1] *Zeit. physikal. Chem.*, 1899, **29**, 613.

[2] *Journ. Chem. Soc.*, 1856, 14.

[3] *Journ. Chem. Soc.*, 1903, 380.

exposed to direct sunlight it is, if sufficiently dilute, gradually converted into hydrochloric acid with evolution of oxygen:

$$Cl_2 + 2H_2O = 4HCl + O_2.$$

It has been proposed to employ this reaction in measuring the chemical action of light, but the decomposition is not sufficiently regular for this purpose; thus Pedler[1] has shown that a solution containing 1 molecule of chlorine to 64 of water undergoes no appreciable alteration during two months' exposure to tropical sunlight, whilst more dilute solutions undergo more or less decomposition, as shown in the following table:—

Mols. H_2O for 1 mol. Cl_2.	Percentage of Chlorine acting on water.
64	no action
88	29
130	46
140	29
412	78

In the case of more dilute solutions, the reaction in sunlight appears to take place almost completely in accordance with the above equation, except in so far as small quantities of chloric acid are formed. In diffused daylight, however, a considerable quantity of the latter acid is obtained, so that in this case the reactions are probably those put forward by Popper,[2]

$$Cl_2 + H_2O = HCl + HClO.$$
$$8HClO = 2HClO_3 + 6HCl + O_2.$$

Under certain conditions, however, sunlight brings about the reverse change, causing the formation of free chlorine from a mixture of hydrogen chloride and oxygen (see p. 194).

CHLORINE AND HYDROGEN.

Hydrochloric Acid, Hydrogen Chloride, or Muriatic Acid. $HCl = 36·18$.

103 The Latin Geber was acquainted with hydrochloric acid in its mixture with nitric acid forming *aqua regia*, which was obtained by distilling nitre, sal-ammoniac, and vitriol together,

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[1] *Journ. Chem. Soc.*, 1890, 613.

[2] *Annalen*, 1885, **227**, 161.

but the first mention of the pure acid under the name of "spiritus salis," prepared from "guter vitriol" and "sal commune," occurs in the supposed works of Basil Valentine. Glauber first obtained this acid by the action of sulphuric acid on common salt about the year 1648, and Stephen Hales, in his work on *Vegetable Staticks*, published in 1727, observed that a large quantity of a gas which was soluble in water was evolved when sal ammoniac and oil of vitriol were heated together. It was not, however, until Priestley[1] collected the gas thus evolved over mercury, by using this metal instead of water in a pneumatic trough, that the gaseous hydrochloric acid was first prepared, and to this gas Priestley gave the name of *marine-acid air*, as calling attention to its production from sea-salt. Lastly, Davy in 1810 proved that the gas, which had been considered to be an oxygen compound, was entirely composed of chlorine and hydrogen.

Hydrochloric acid gas, the only known compound of chlorine and hydrogen, occurs in the exhalations from active volcanoes,[2] especially in Vesuvius,[3] and in the fumeroles on Hecla.[4] In aqueous solution, the acid has been found in the waters of several of the South American rivers rising in the volcanic districts of the Andes. It is also found in small quantities in the gastric juice of man and other animals.

104 Hydrochloric acid can be formed by the union of its constituent elements. If equal volumes of chlorine and hydrogen be mixed together, no combination occurs so long as the mixture remains in the dark and at the ordinary atmospheric temperature; but if the moist mixed gases be exposed to a strong light, or if a flame be brought to the mouth of the jar, or an electric spark passed through the gases, a sudden combination takes place, the heat suddenly evolved by the union of the chlorine and hydrogen being sufficient to produce a violent explosion. In order to exhibit this singular action of light, inducing the combination of chlorine and hydrogen, a small thin flask may be filled, in a darkened room, half with chlorine gas (by displacement over hot water) and half with hydrogen. The flask, corked and covered up, may then be exposed either to sunlight, or to the bright light of burning magnesium

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[1] *Observations on Different Kinds of Air*, 1772, vol. iii. 208.

[2] *Pseudo-Volcanic Phenomena of Iceland*, *Cav. Soc. Mem.*, p. 327.

[3] Palmieri, *The Late Eruption of Vesuvius*, 1872, p. 136.

[4] Bunsen, *Annalen*, 1847, **62**, 1.

ribbon, when a sharp explosion will instantly occur, the flask will be shattered, and fumes of hydrochloric acid will be seen.

A better method of showing this combination is to obtain a mixture of exactly equivalent volumes of chlorine and hydrogen by the electrolysis of aqueous hydrochloric acid itself.[1] For this purpose an apparatus shown in Fig. 46 is employed; this consists of an upright glass tube filled with about 120 cc. of pure fuming aqueous hydrochloric acid, containing about 30 per cent. of HCl. Two poles of dense carbon, as used for the electric arc lamp, pass through tubulures in the sides of the glass, being fastened in their place by means of caoutchouc stoppers. The apparatus having been brought into a room lighted only by a candle or small gas flame, the carbon poles are connected with three or four Bunsen's elements, the current from which is allowed to pass through the liquid. At first gas is evolved from the negative pole only, and this consists of hydrogen, whilst all the chlorine, which is evolved at the positive pole, is absorbed by the liquid. After the evolution has gone on for two or three hours the liquid becomes saturated with chlorine, and the gases are given off at each pole in exactly equivalent volumes, and consist of hydrogen and chlorine. The gaseous mixture thus obtained is washed by passing through a few drops

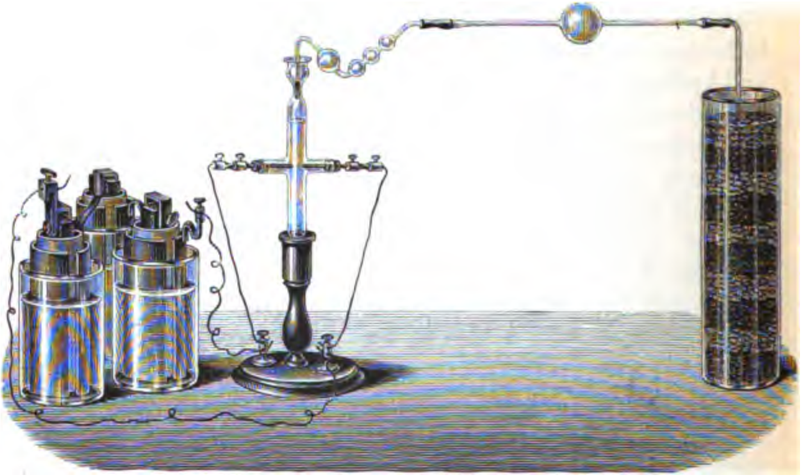

FIG. 46.

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[1] Roscoe, *Journ. Chem. Soc.*, 1856, 16.

of water contained in the bulb-tube ground into the neck of the evolution vessel, and then passes into a thin glass bulb, of about the size of a hen's egg, blown on a piece of easily fusible tubing. At each end the tube is drawn out so as to be very thin in the glass, and to have the internal diameter not greater than 1 mm., whilst at the extremities the tube is wider, so as to fit ordinary caoutchouc joinings. In order to absorb the excess of chlorine the further end of the bulb is placed in connection with a condenser containing slaked lime and charcoal placed in alternate layers. The mixed gas thus obtained is free from oxides of chlorine, but contains a small quantity of oxygen, averaging about 0·1 c.c. per litre.[1]

When the gas has passed through the bulb-tube (at the rate of about two bubbles every second) for about ten minutes, the joinings are loosened and each end stopped by a piece of glass rod. In order to preserve the gaseous mixture, which is unalterable in the dark for any length of time, the bulbs are hermetically sealed. For this purpose the thinnest part of the tube is brought some little distance above a very small flame from a Bunsen burner: the glass softens below a red heat, and the ends may be drawn out and sealed with safety. It is, however, advisable to hold the bulb in a cloth during the operation of sealing, as not infrequently the gas explodes. As soon as one bulb is removed a second is introduced, and placed in connection with the evolution flask, and after ten minutes sealed as described. The bulbs thus obtained should be numbered, and the first and last tested by exposing them to a strong light, and if these explode, all the intermediate bulbs may be considered good. Sixty such bulbs may be prepared with the above quantity of acid, and may be kept in the dark for an unlimited time without change.[2] On exposing one of these bulbs to the light emitted by burning magnesium ribbon, or to bright daylight, a sharp explosion occurs and hydrochloric acid is formed (Fig. 47).

105 *Mechanism of the Combination of Hydrogen and Chlorine.* During the past 60 years a number of investigations have been made to ascertain the exact manner in which the combination of hydrogen and chlorine takes place, and the part played by light rays in the reaction; but whilst results of great interest have been obtained, the matter has not yet been fully elucidated.

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[1] Mellor, *Journ. Chem. Soc.*, 1901, 222.

[2] Roscoe, *Proc. Manch. Lit. and Phil. Soc.*, Feb. 1865.

In 1843, Draper[1] observed that when the light from an electric spark is allowed to fall on a mixture of equal volumes of hydrogen and chlorine gases, the mixture suddenly expands, and then returns to its original volume. The further investigation of this phenomenon by Mellor[2] has shown that the expansion is due to the light rays only, and that these bring about the formation of hydrochloric acid in limited quantity, the expansion being due to the heat of combination, the gases therefore returning to their original volume as the heat is dispersed. The amount of combination depends on the number and intensity of the sparks, and when the effect reaches a certain magnitude, dependent upon the sensibility of the mixture, explosion occurs.

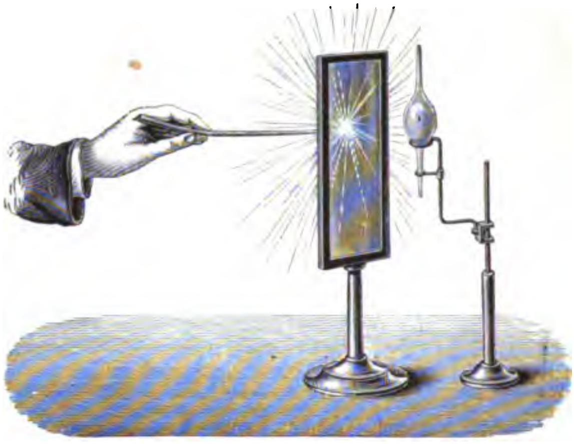

FIG. 47.

When the mixture of hydrogen and chlorine is exposed to diffused daylight, combination gradually takes place, the rate of formation of hydrochloric acid increasing with an increasing proportion of the more refrangible rays of light. Bunsen and Roscoe[3] found, however, that the action of light is at first very slow, and only attains its full activity after a certain length of time. Thus, for example, when a mixture of the gases was exposed to the light of a small petroleum lamp burning at a constant rate it was found that the amount of hydrochloric

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[1] *Phil. Mag.*, 1843 [3], **23**, 403, 415.

[2] *Journ. Chem. Soc.*, 1902, 414.

[3] *Phil. Trans.*, 1857.

acid formed in each minute increased for the first nine minutes and then became constant. To this phenomenon they have given the name "photo-chemical induction."

In 1887, Pringsheim[1] showed that when the mixed gases are dried, the action of light of given intensity is much less marked than with the moist gases, and concluded that the combination of the two elements does not take place directly, but that in the first place an intermediate compound is produced by the action of light, in the formation of which the moisture present takes part, and that this intermediate compound then reacts with either hydrogen or chlorine yielding hydrochloric acid and re-forming water, which is again acted on with production of the intermediate compound. Under these circumstances the existence of the "period of induction" is what would be expected; thus during the first period of the action of light the amount of hydrochloric acid formed would be small, because the formation of the acid could only take place after a certain quantity of the intermediate compound had been produced; after a time, however, the quantity of the intermediate compound formed would be equal to the quantity decomposed, and the amount of the latter in the mixture and of the hydrochloric acid formed in a given time would remain constant. The first period corresponds to the period during which "induction" takes place, and the second to that in which the light brings about the formation of the product of the reaction at a constant rate.

Further confirmation of this hypothesis is found in the observation of H. B. Baker,[2] that when a highly dried mixture of pure hydrogen and chlorine is exposed to daylight the combination takes place exceedingly slowly, 25 per cent. of the gas remaining uncombined after exposure for two days to diffused daylight, and two days to bright sunshine.

Such an intermediate compound, if formed, would only be present at any time in very small quantity, and no direct proof of its existence has as yet been found. The recent confirmation of Draper's statement (p. 181), that moist chlorine which has been previously exposed to light combines more readily with hydrogen than the unexposed chlorine, renders it probable that only the chlorine and the moisture and not the hydrogen are concerned in its production. This is further confirmed by the

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[1] *Ann. Phys. Chem.*, 1887 [2], **32**, 384.

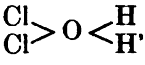
[2] *Journ. Chem. Soc.*, 1894, 612.

observation of Mellor,[1] that when a mixture of hydrogen and chlorine is prepared by the electrolysis of hydrochloric acid, and the chlorine exposed to the light of an acetylene flame or to the action of a silent electric discharge previous to mixing with the hydrogen, the period of induction required for the attainment of a constant rate of formation of hydrochloric acid from the mixed gases is less than two minutes, as compared with six minutes when the chlorine has not been subjected to any previous treatment. Pringsheim has suggested that the intermediate compound is chlorine monoxide, the reactions representing the combination being then

$$(1)\ H_2O + Cl_2 = Cl_2O + H_2,$$
$$(2)\ 2H_2 + Cl_2O = 2HCl + H_2O,$$

whilst Becquerel,[2] Veley,[3] and Gautier and Helier[4] regard hypochlorous acid as the intermediate substance,

$$(1)\ H_2O + Cl_2 = HClO + HCl,$$
$$(2)\ HClO + H_2 = H_2O + HCl.$$

If either of these suppositions is correct, the addition of chlorine monoxide or of hypochlorous acid to the mixed gases should shorten the period of induction; but Mellor[5] has proved that this is not the case, and Burgess and Chapman[6] have further shown that a mixture of the gases which has passed through the period of induction can be rendered inactive by shaking with water, hydrochloric acid, hypochlorous acid, or chlorine water, and both the above suggestions are therefore untenable. Bevan[7] has suggested that the intermediate compound is one formed by the direct union of one molecule of chlorine and one of water, having the constitution  $\begin{smallmatrix}Cl\\Cl\end{smallmatrix}\!>O<\!\begin{smallmatrix}H\\H\end{smallmatrix}$, and that this reacts with hydrogen forming hydrochloric acid and water.

Combination of hydrogen and chlorine also takes place when the mixed gases are heated to a sufficiently high temperature: in closed vessels explosion occurs between 240° and 270°, whereas if the mixture is passed in a stream through the heated vessel

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[1] *Proc. Chem. Soc.*, 1904, 140.
[2] *Wurtz Dict.*, 1879, **2**, 255.
[3] *Phil. Mag.*, 1894 [5], **37**, 170.
[4] *Compt. Rend.*, 1897, **124**, 1268.
[5] *Journ. Chem. Soc.*, 1902, 1292.
[6] *Proc. Chem. Soc.*, 1904, 52, 164.
[7] *Phil. Trans.*, 1903, **202**, 71.

the explosion does not take place till the temperature reaches 430° to 440°.[1]

106 Hydrochloric acid is also formed by the action of chlorine upon almost all hydrogen compounds, which are decomposed by it either in the dark or in presence of light; thus sulphuretted hydrogen, olefiant gas, turpentine (see p. 179), and water, are all decomposed by chlorine, hydrochloric acid being formed. When hydrogen is passed over certain metallic chlorides, such as silver chloride, hydrochloric acid is evolved, and the metal produced, thus:—

$$2AgCl + H_2 = 2Ag + 2HCl.$$

By these and other reactions hydrochloric acid is frequently formed; but none of them serve for the preparation of the gas on a large scale.

Preparation.—For this purpose six parts by weight of common salt are introduced into a capacious flask, and eleven parts of strong sulphuric acid slowly poured on it through a bent tube-funnel; the gas, which is at once rapidly evolved, is purified from any sulphuric acid or salt which may be carried over, by passing through a small quantity of water contained in a wash bottle, and it may then either be collected by displacement (like chlorine), or over mercury, or passed into water, as shown in Fig. 52, if an aqueous solution of the acid is needed.

The reaction which here occurs is represented by the equation:

$$NaCl + H_2SO_4 = HCl + NaHSO_4.$$

Hydrochloric acid comes off, and the readily soluble hydrogen sodium sulphate, $NaHSO_4$, is left. If two molecules of salt be taken to one of sulphuric acid, a less easily soluble salt, normal sodium sulphate, Na_2SO_4, is formed, a greater heat being needed to complete the decomposition than when an excess of acid is employed, thus:—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

107 *Properties.*—Hydrochloric acid is a colourless gas, which was first liquefied by Davy and Faraday,[2] by allowing sulphuric acid to act on ammonium chloride in a sealed and bent tube; after a time the pressure becomes sufficiently great to liquefy the

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[1] Freyer and V. Meyer, *Zeit. physikal. Chem.*, 1893, **11**, 28.

[2] Davy and Faraday, *Phil. Trans.*, 1823, p. 164.

further portions of the gas which are evolved, and by gentle heat the liquid may be distilled over into the empty limb of the tube. It is a colourless liquid, has a specific gravity of 0·854 at − 105°, and solidifies to a crystalline mass which melts at − 112°·5 (Olszewski), and does not conduct electricity. The liquid has a vapour pressure of 29·8 atm. at 4°, and 41·8 atm. at 18·1°, the critical temperature being 52·3°, and the critical pressure 86 atm. The action of liquid hydrochloric acid upon various substances has been carefully examined by Gore,[1] whose experiments show that the liquid acid has but a feeble solvent power for bodies in general, and, with the exception of aluminium, does not attack the metals.

Hydrochloric acid gas is heavier than air. Its specific gravity, according to the experiments of Biot and Gay-Lussac, is 1·278 (air = 1), whilst according to Leduc [2] it is 1·2692, or its density is 18·39 (H = 1), the calculated density being 18·09. At 1,500° the gas appears to have undergone no change, but at 1,700° a considerable amount of dissociation has taken place.[3] The gas fumes strongly in the air, uniting with atmospheric moisture, and it is instantly absorbed by water or ice, yielding the aqueous acid. It possesses a strongly acid reaction and suffocating odour, and is not inflammable. A burning candle is extinguished when plunged into the gas, the outer mantle of the flame, before extinction, exhibiting a characteristic green coloration.

Direct sunlight has no action on a dry mixture of hydrogen chloride and oxygen, but if more moisture than is necessary for the complete saturation of the gas be present, decomposition gradually takes place, free chlorine and water being formed. The amount of chlorine liberated depends upon the proportion of oxygen present; thus a mixture of 4 volumes of hydrogen chloride and 1 volume of oxygen only gave 0·34 per cent. of free chlorine after 24 days' exposure, whilst with 8 volumes of oxygen 73·81 per cent. of the chlorine was liberated. It appears that in some cases hypochlorous acid is also formed.[4]

108 The composition of hydrochloric acid gas can be best ascertained as follows:—

Metallic sodium decomposes the gas into chlorine, which

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[1] *Proc. Roy. Soc.*, 1865, **14**, 204.

[2] *Comptes Rend.*, 1897, **125**, 571.

[3] Langer and V. Meyer, *Pyrochem. Unters.* (Vieweg), p. 67.

[4] McLeod, *Journ. Chem. Soc.*, 1886, 591; Richardson, *Journ. Chem. Soc.*, 1887, 802.

combines with the metal to form sodium chloride, and into hydrogen, which is liberated. If a small piece of sodium be heated in a deflagrating spoon until it begins to burn, and then plunged into a jar of hydrochloric acid gas, the combustion of the metal (union with chlorine) will go on in the gas. In order to show what volume of hydrogen is evolved from a given volume of hydrochloric acid gas by this reaction, the following experiment may be made with the eudiometer tube, the construction of which is clearly seen in Fig. 48. To begin with, both limbs are filled completely with dry mercury, then the end of the tube carrying the stopcock is connected by a piece of caoutchouc tubing with an evolution flask, from which pure hydrochloric acid gas is being slowly evolved from a mixture of dry

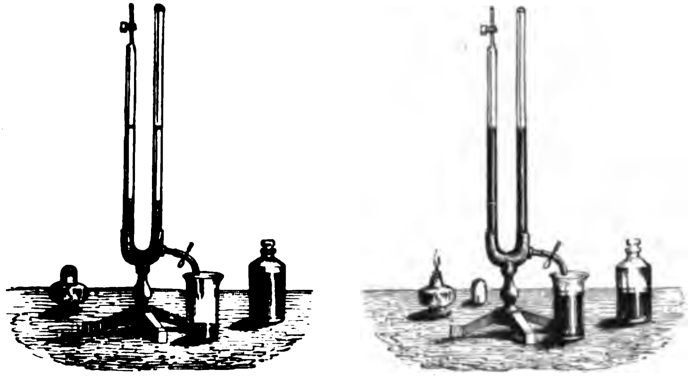

FIG. 48.

salt and strong sulphuric acid, care being taken that the air has been driven out. On turning the stopcock at the top of the tube, and opening the screw-tap on the caoutchouc in the U-tube, the mercury will run out, and dry hydrochloric acid gas will enter the one limb, whilst air fills the other to the same level. As soon as the gas reaches a mark on the tube indicating that it is two-thirds full of gas the stopcock is closed. A small quantity of sodium amalgam is now prepared by pressing six or eight small pieces of clean cut sodium, one by one, under the surface of a few ounces of mercury contained in a porcelain mortar. The amalgam is then poured into the open limb of the U-tube so as to fill it, and the end firmly closed with the thumb; the hydrochloric acid gas is now transferred to the limb containing the amalgam, and well shaken so as to bring the gas and amalgam into contact. The gas is next passed back into the closed limb, and the pressure equalised by bringing the mercury in both limbs to the same level, which is easily done by allowing some mercury to flow out by loosening the screw-tap at the bottom of the U-tube. The hydrochloric acid gas will be completely decomposed by contact with sodium amalgam, chloride of sodium being formed, whilst the hydrogen is left in the gaseous state. This will be found to occupy exactly half the volume of the original gas, the level of the mercury having risen to a mark previously made and indicating exactly one-third of the capacity of the tube. As the closed limb is provided with a stopcock, the residual gas may be inflamed, and thus shown to be hydrogen.

It still, however, remains to ascertain the volume of the chlorine which has disappeared. This is done as follows:—Two glass tubes about 50 cm. long and 1·5 cm. in diameter, drawn out at each end to a fine thread, are filled with the gaseous mixture evolved by the electrolysis of the aqueous acid (see p. 188). The process is conducted exactly as if a bulb were being filled, and the tubes are then sealed up and kept in the dark. When it is desired to exhibit the composition of the gas, one of the tubes thus filled is brought into a dimly-lighted room, and one of the drawn-out ends broken under mercury. No alteration in the bulk of the gas will be noticed. The mercury in which the tube dips is now replaced by a colourless solution of iodide of potassium, and, by giving the tube a slight longitudinal shaking, a little of this solution is brought in contact with the gas. No sooner does the liquid enter the tube than it becomes of a dark brown colour, due to the liberation of the iodine, the chlorine uniting with the potassium to form the chloride of that metal. A consequent diminution of bulk occurs which corresponds precisely to the volume of chlorine contained in the tube, and in a few moments the column of liquid fills half the tube, proving that half the volume of the mixed gas consists of chlorine, and the other half of hydrogen. We have, however, learnt from the previous experiment that hydrochloric acid gas contains half its own volume of hydrogen, so that we have now ascertained (1) that hydrochloric acid gas is entirely made up of equal volumes of chlorine and hydrogen, and (2) that these elementary components combine together without change of volume to produce the compound hydrochloric acid gas.

This fact may be further illustrated by exposing a second sealed-up tube, containing the electrolytic gas, for a few minutes, first to a dim, and then to a stronger daylight. The greenish colour of the chlorine will soon disappear, a gradual combination of the gases having occurred. On breaking one end of the tube under mercury, no alteration of bulk will be observed, whilst on raising the open end into some water poured on the top of the mercury, an immediate and complete absorption will be noticed, and the tube will become filled with water.

In order to determine with a greater degree of exactitude than is possible by the above methods the relation existing between the two gases, a quantitative analysis of the chlorine contained in a given volume of the electrolytic gas must be made. Two experiments thus conducted gave the following results:—

	I.	II.	Calculated.	
Chlorine ...	49·85 ...	50·02 ...	50·00	volumes.
Hydrogen...	50·15 ...	49·98 ...	50·00	„
	100·00	100·00	100·00	

Showing that the gas obtained by decomposing aqueous hydrochloric acid consists exactly of equal volumes of chlorine and hydrogen, or

$$\tfrac{1}{2} \text{ vol. of chlorine weighing } \frac{35·18}{2} = 17·59$$

$$\tfrac{1}{2} \quad „ \quad \text{hydrogen} \quad „ \quad \frac{1}{2} = 0·50$$

$$\text{1 vol. of hydrochloric acid weighing } \ldots \; 18·09$$

109 Hydrochloric acid gas is very soluble in water, and the solution is largely used for laboratory and for commercial purposes, and frequently termed muriatic acid. In order to exhibit the solubility of the gas in water, a large glass globe (Fig. 49) placed on a stand is filled, by displacement, with the gas; a tube, reaching to the centre of the globe and dipping to the bottom of an equal-sized globe placed beneath, being fixed in a caoutchouc stopper placed into the neck of the upper globe. Between the two globes the tube is joined by a piece of caoutchouc tubing, closed by a screw-tap. When it is desired to show the absorption, the lower globe is filled with water coloured blue by infusion of

litmus, the screw-tap is opened and a little of the water forced into the upper globe (so as to begin the absorption) by blowing through the side tube into the space above the surface of the liquid in the lower globe. As soon as the water makes its appearance at the top of the tube, a rapid absorption occurs, the liquid rushes up in a fountain, and at the same time becomes coloured red.

Fig. 49.

110 *Manufacture of Hydrochloric Acid.*—This acid is obtained on the large scale as a bye-product in the manufacture of soda-ash (Vol. II. [1897], p. 192). In the alkali works 10 cwt.

of salt is introduced into a large hemispherical iron pan, 9 feet in diameter, heated by a fireplace underneath, and covered

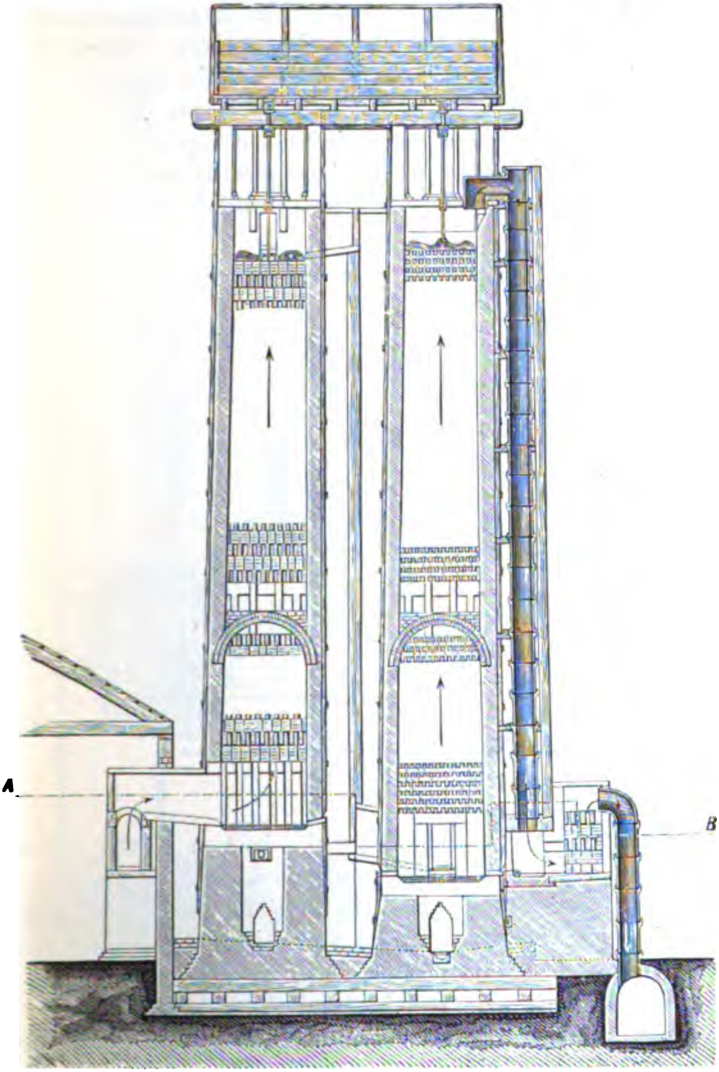

Fig. 50.

by a brickwork dome; upon this mass of salt the requisite quantity (10 cwt.) of sulphuric acid (sp. gr. 1·7) is allowed to run from a leaden cistern placed above the decomposing pan. Torrents of hydrochloric acid gas are evolved, which collect in the space between the pan and the brickwork dome, whence they pass by a brickwork or earthenware flue into upright towers or condensers, built of bricks soaked in tar, or of Yorkshire flags fitted and clamped together. These towers, shown in vertical section in Fig. 50, and in ground plan in Fig. 51, are filled with bricks or coke, down which a small stream of water, from a reservoir at the top of the tower, is allowed to trickle. The gas passing upwards, as shown in the figures by the arrow, meets the water and is dissolved by it; and as the acid-liquor approaches the bottom of the tower it becomes more and more nearly saturated with the gas.

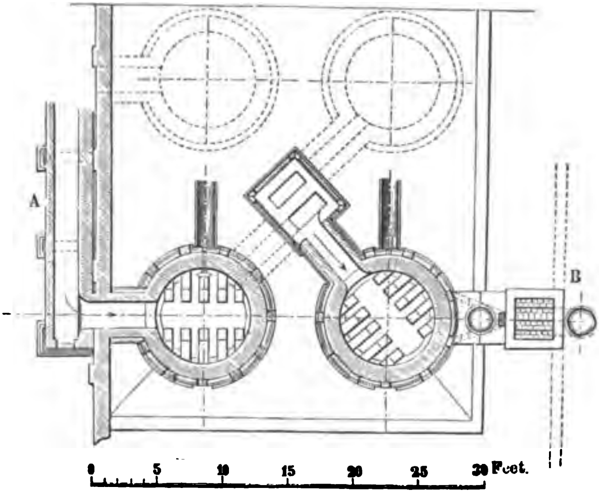

FIG. 51.

The aqueous commercial acid thus obtained from impure materials is generally far from pure; it is usually of a yellow colour, due to organic matter, and may also contain sulphur dioxide, sulphuric acid, chlorine, and the chlorides of iron and of arsenic: this last is often present in large quantities, being derived from the pyrites used in making the sulphuric acid.

The presence of arsenic may be detected by Marsh's reaction; or by the addition of stannous chloride, which produces a brown precipitate of impure arsenic. To remove traces of arsenic, solution of stannous chloride may be added, the precipitate allowed to settle, and the clear liquid re-distilled. Free chlorine may be detected by the addition to the diluted acid of pure iodide of potassium and starch solution, when if chlorine be present the blue iodide of starch will be formed. The presence of sulphuric acid can be easily ascertained by adding chloride of

FIG. 52.

barium solution to the diluted acid, whilst that of sulphurous acid may be shown by adding zinc to the diluted acid, when sulphuretted hydrogen will be given off, and its presence readily ascertained by its blackening action on lead paper. It is, however, not easy to separate these substances so as to obtain a strong pure acid from one originally impure, and by far the simplest plan is to exclude the foreign matters by employing pure materials to begin with.

III The pure saturated aqueous acid is a colourless liquid fuming strongly in the air. It is prepared for laboratory use by means of the apparatus shown in Fig. 52. One volume of water at 0° absorbs 503 times its volume of hydrochloric acid gas. The weight and volume of the gas absorbed under the pressure of 760 mm. by one gram of water at different temperatures is given in the following table.[1]

Temp.	Grms. HCl.	Temp.	Grms. HCl.
0°	0·825	32°	0·665
4	0·804	36	0·649
8	0·783	40	0·633
12	0·762	44	0·618
16	0·742	48	0·603
20	0·721	52	0·589
24	0·700	56	0·575
28	0·682	60	0·561

The weight of gas dissolved under changing pressure (the temperature remaining constant) does not vary proportionally to the pressure, and, therefore, this gas does not follow Dalton and Henry's law. Thus, for instance, under the pressure of 1 metre of mercury 1 grm. of water dissolves 0·856 grm. of the gas; according to Dalton and Henry's law the weight of gas absorbed under a pressure of 1 decimetre of mercury should be 0·0856 grm., whereas it is found to be 0·657 grm.

On heating a saturated solution of the gas in water having a specific gravity of 1·22, a distillate is obtained which is richer in HCl than the original liquid, and the residue therefore gradually becomes weaker. On the other hand, the distillate from a dilute acid is weaker than the original, and the residue becomes stronger, so that at last both the strong acid and the weak acid reach the same strength, and both when boiled distil over unchanged, provided the pressure does not vary. The aqueous acid, which boils unchanged at 110° under the normal pressure, contains 20·24 per cent. of hydrochloric acid, HCl.[2] If the distillation proceeds under a greater or less pressure than the normal,

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[1] Roscoe and Dittmar, *Journ. Chem. Soc.*, 1860, 128.

[2] Roscoe and Dittmar, *loc. cit.*

distillates of constant composition are obtained, but each one contains a different quantity of hydrochloric acid. This is clearly seen from the following table.

Column I. gives the pressure in metres of mercury under which distillation was conducted; Column II. the percentage of hydrochloric acid (HCl) found in the residual acid.

I.	II.	I.	II.	I.	II.
0·05	23·2	0·8	20·2	1·7	18·8
0·1	22·9	0·9	19·9	1·8	18·7
0·2	22·3	1·0	19·7	1·9	18·6
0·3	21·8	1·1	19·5	2·0	18·5
0·4	21·4	1·2	19·4	2·1	18·4
0·5	21·1	1·3	19·3	2·2	18·3
0·6	20·7	1·4	19·1	2·3	18·2
0·7	20·4	1·5	19·0	2·4	18·1
0·76	20·24	1·6	18·9	2·5	18·0

Here the percentage of the acid and the constant composition obtained by distillation under a pressure of 0·5 decimetre is seen to be 23·2 HCl; whereas when the pressure is increased to 2·5 metres the percentage of the acid of constant boiling-point is 18·0 HCl. In the same way, if dry air is passed through aqueous hydrochloric acid a part of the acid is vaporised and a residue is obtained which for each given temperature remains of constant composition. An acid weaker or stronger than this ultimately attains this composition.

The following table shows the composition of the constant aqueous hydrochloric acids obtained by leading air at given temperatures through the liquid.

Temp.	Per Cent. of HCl.	Temp.	Per Cent. of HCl.
0°	25·0	60°	23·0
10	24·7	70	22·6
20	24·4	80	22·0
30	24·1	90	21·4
40	23·8	100	20·7
50	23·4		

Hence it is seen that an aqueous acid which boils unaltered under a given pressure, and, therefore, at a constant temperature, contains the same percentage of HCl as the constant acid obtained by passing dry air through the aqueous acid. Thus the boiling-point of the acid under 0·1 metre of pressure, containing 22·9 per cent. of HCl, is from 61° to 62°; and if dry air be passed through an aqueous acid at 62° the constant point is attained when the liquid contains 22·9 per cent. of HCl.

These solutions of HCl in water, having a constant boiling-point, must be regarded as physical mixtures, and not as true chemical compounds, inasmuch as they undergo a change in composition when the pressure under which they are distilled is modified, however slight the alteration. The characteristic of a chemical compound is that it preserves its constant composition throughout a definite range of temperature or pressure.

The following table gives the specific gravity of solutions of aqueous hydrochloric acids of varying strengths, according to the experiments of Lunge and Marchlewski.[1]

Percentage of HCl.	Specific Gravity at 15° compared with water at 4°.	Percentage of HCl.	Specific Gravity at 15° compared with water at 4°.
1·52	1·0069	22·89	1·1150
2·93	1·0140	25·18	1·1271
5·18	1·0251	27·75	1·1405
7·84	1·0384	29·35	1·1490
9·99	1·0491	31·28	1·1589
12·38	1·0609	33·39	1·1696
15·84	1·0784	35·36	1·1798
17·31	1·0860	37·23	1·1901
18·36	1·0914	39·15	1·2002
20·29	1·1014		

From these numbers the percentage of any acid of known specific gravity can easily be found by interpolation.

Hydrates of Hydrochloric Acid.—When a saturated aqueous solution of hydrochloric acid is cooled below −40° it freezes to a butter-like mass, having the composition $HCl, 2H_2O$. This hydrate also separates from solutions containing from 43·93 to 48·81 per cent. of HCl at temperatures between −26°·25 and − 17°·5, whilst from solutions containing from 25·1—42·5 per cent. the *trihydrate* $HCl, 3H_2O$ separates out between −80° and −25°·65.[2]

112 *The Chlorides.*—Certain metals enter very readily into combination with chlorine, heat being always evolved, and the phenomena of combustion frequently observed. Other metals again do not combine so easily. Most of the metallic chlorides

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[1] *Zeit. angew. Chem.*, 1891, 133.

[2] Pickering, *Ber.*, 1893, **26**, 277.

are soluble in water; amongst those insoluble are silver chloride $AgCl$, mercurous chloride (calomel) $HgCl$, and cuprous chloride Cu_2Cl_2. Many metals combine in more than one proportion with chlorine, thus we find:

Cuprous Chloride, Cu_2Cl_2,	Cupric Chloride, $CuCl_2$.
Mercurous Chloride, $HgCl$,	Mercuric Chloride, $HgCl_2$.
Tin Dichloride, $SnCl_2$,	Tin Tetrachloride, $SnCl_4$.
Platinum Dichloride, $PtCl_2$,	Platinum Tetrachloride, $PtCl_4$.
Ferrous Chloride, $FeCl_2$,	Ferric Chloride, $FeCl_3$.

The chlorides of the metals are usually prepared by one of the following processes, which are typical methods for the preparation of the salts of any acid:—(1) By acting on the metal with chlorine gas, especially when the anhydrous chloride is required. (2) By the action of chlorine upon metallic oxides, when it drives off the oxygen and unites with the metal to form a chloride. (3) By acting on the metal with hydrochloric acid. (4) By dissolving the oxide, hydrate, or carbonate of the metal in hydrochloric acid. (5) In certain cases, by adding a soluble chloride to a solution of a salt of the metal, when the metallic chloride is obtained as an insoluble precipitate.

Chlorine also unites with all the non-metallic elements, except those of the helium group, and with certain groups of atoms termed radicals, to form chlorides of these elements and radicals respectively, some examples of which are as follows:—

Non-Metallic Chlorides.

Hydrochloric Acid	HCl.
Chloride of Sulphur	S_2Cl_2.
Trichloride of Boron	BCl_3.
Tetrachloride of Silicon	$SiCl_4$.
Pentachloride of Phosphorus	PCl_5.

Chlorides of Inorganic Radicals.

Chloride of Sulphuryl	SO_2Cl_2.
Chloride of Phosphoryl	$POCl_3$.

Chlorides of Organic Radicals.

Chloride of Ethyl	C_2H_5Cl.
Chloride of Ethylene	$C_2H_4Cl_2$.
Chloride of Acetyl	C_2H_3OCl.
Chloride of Cyanogen	$CNCl$.

113 *Detection and Estimation of Chlorine and Chlorides.*—In the free state chlorine gas is recognised by its peculiar colour, its suffocating smell, and by its bleaching action on organic colouring matters. When present in smaller quantities, its presence may be detected by the blue colour which it causes on a paper moistened with a solution of iodide of potassium, KI, and starch paste, owing to the fact that chlorine liberates iodine from its compound with potassium, combining with the metal to form the chloride, KCl, whilst the liberated iodine forms a deep blue compound with starch. This reaction is very delicate, but it must be remembered that an excess of chlorine again removes the blue colour, and also that the same effect is produced by bromine, nitrous fumes, ozone, and other oxidising substances.

Chlorides soluble in water are usually detected by the formation of the curdy white precipitate of silver chloride, AgCl, on addition of a solution of silver nitrate, $AgNO_3$, to that of a soluble chloride, such as KCl, thus:—

$$KCl + AgNO_3 = AgCl + KNO_3.$$

One part of chlorine in one million parts of water can thus be detected—a faint opalescence occurring. The precipitated silver chloride becomes violet-coloured on exposure to light, and is insoluble in water and dilute acids, especially nitric acid, but readily soluble in ammonia and in solutions of potassium cyanide and sodium thiosulphate (often called hyposulphite of soda). Mercurous nitrate likewise produces in solutions of a chloride a white precipitate of mercurous chloride (calomel), which does not dissolve, but turns black, on addition of ammonia.

In order to detect a chloride in presence of an iodide and bromide, the dried salt is distilled with potassium chromate and strong sulphuric acid, when chromium oxychloride, CrO_2Cl_2, distils over as a dark red liquid, decomposed by addition of water or ammonia, yielding a yellow solution which, on addition of hot acetic acid and a soluble lead salt, gives a yellow precipitate of lead chromate; neither bromine nor iodine forms a similar compound with chromium, but these elements are liberated by this treatment. Chlorine, when combined to form a chloride, is always estimated as silver chloride, AgCl, and according to Stas 142·30 of silver chloride contain 35·18 of chlorine. If the chlorine is present in the free state it can be determined by volumetric analysis (see *Chlorimetry*, under *Bleaching Powder*, Vol. II. 1897, p. 435), or it may be reduced by sulphur dioxide, SO_2, to hydrochloric acid, and then precipitated as silver chloride and weighed.

The atomic weight of chlorine was first determined by Berzelius,[1] together with that of silver and potassium. Penny[2] and Marignac[3] have also made similar determinations; the latter obtaining the numbers 35·197 and 35·179 by methods similar to those employed by Berzelius. It is to Stas[4] that we owe the most exact determinations. He converted pure silver into silver chloride by four different methods, and found as the mean of closely-agreeing results that the relation of the weight of silver to that of the silver chloride it yields is 1 : 1·3285. It is further known that the relation of the atomic weights of silver and oxygen is 6·7456 : 1, this ratio having been also obtained from a large number of experiments, such, for example, as the ratios of equivalent quantities of the following:—

$$Ag_2S : Ag_2SO_4 \text{ and } AgCl : AgClO_3.$$

Hence if the atomic weight of oxygen is taken as 15·88 that of chlorine is 35·18.

BROMINE. Br. = 79·36. H = 1.
= 79·96. O = 16.

114 **Bromine** does not occur in the free state in nature; it was discovered in the year 1826 by Balard,[5] who prepared it from the liquor called bittern, remaining after the common salt has crystallised out from concentrated sea-water, in which it occurs combined with metals to form bromides; he gave it the name from *βρῶμος*, a bad smell.

Bromine occurs in combination with silver in certain ores, from Mexico, Chili, and Bretagne; but is found in large quantities (combined with sodium, potassium, magnesium, or calcium, forming *bromides*) in the water of many mineral springs, some of which contain enough to serve as a source of this element. It is also found, though in very small quantity, in all sea-water,[6] and has been detected in seaweed from many

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[1] *Pogg. Ann.*, 1826, **8**, 1.

[2] *Phil. Trans.*, 1839, p. 20.

[3] *Annalen*, 1842, **44**, 11; *Bibl. Univ. de Genève*, **43**, 350.

[4] *Recherches sur les Lois des Proportions Chimiques*, Bruxelles, 1865.

[5] *Ann. Chim. Phys.*, 1826 [2], **32**, 337.

[6] The water of the Dead Sea is said to contain large quantities, of no less than 0·42 gram in the litre (Lartet).

localities, and even in certain marine animals, as well as in English rock-salt. The mineral springs at Kreuznach, Kissingen, and Schönebeck, and the potash beds of Stassfurt, as well as certain American springs in Ohio and elsewhere, contain considerable quantities of bromine, the commercial article being obtained almost entirely from the two last-named sources.

115 *Preparation.*—In order to detect bromine in a mineral water, or to prepare it in small quantities, the following method is employed. The mother-liquor remaining after the brine from any of the above sources has been well crystallised is treated with a stream of chlorine gas, so long as the yellow colour of the liquid continues to increase in depth. Chlorine has the power of liberating bromine from bromides, itself uniting with the metal, and the bromine being set free, thus:—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

The addition of excess of chlorine is to be avoided, as a compound of chlorine and bromine is then formed. The yellow liquid is then well shaken with chloroform, which dissolves the bromine, forming, on standing, a brown solution below the aqueous liquid. On adding caustic potash to this solution the colour at once disappears, the bromine combining to form the bromide, KBr, and bromate of potassium, $KBrO_3$, thus:—

$$3Br_2 + 6KHO = KBrO_3 + 5KBr + 3H_2O.$$

On further concentrating the solution a mixture of these salts remains, and from these the bromine is again liberated by distilling the liquid with black oxide of manganese and sulphuric acid in a tubulated retort. The decomposition which here occurs is similar to that which takes place in the preparation of chlorine. Dark red fumes of bromine are liberated, and a black liquid condenses in the well-cooled receiver.

If the bromine is required to be anhydrous it must be re-distilled over concentrated sulphuric acid; and if iodine is present this must be got rid of previously by precipitation as subiodide of copper.

By far the greater quantity of the bromine brought into commerce is now manufactured at Stassfurt from the mother-liquor remaining after the separation of the potassium salts contained in the salt deposits, the process adopted consisting in the treatment of the liquors with chlorine under suitable conditions. The most recent apparatus for this purpose is shown in Fig. 53, and is so arranged that the process is continuous. The mother-liquor enters the apparatus by the hydraulically sealed pipe *a*, and by means of the sandstone drum *b*, and perforated plate *e*, is distributed equally over the whole area of the tower A. The latter is filled with balls over which the liquor flows, thus exposing a large surface to the action of the chlorine gas passing through the tower in the opposite direction; the waste liquor passes away by the pipe *d*, which is sufficiently large to allow of the simultaneous passage of the chlorine gas to the tower from the generator D. In order to free the waste liquor completely from all traces of chlorine and bromine it is run into the vessel B, which is kept full to the bottom of the pipe *d*; to pass away from B the liquor must flow over the sandstone shelves, in the direction shown by the arrows, in doing which it is subjected to the action of a current of high-pressure steam which is introduced into the apparatus by the pipe *g*. All the chlorine and bromine are thus driven out of the liquor and rise to the top of B, where they mingle with the chlorine gas passing from the generator to the tower,

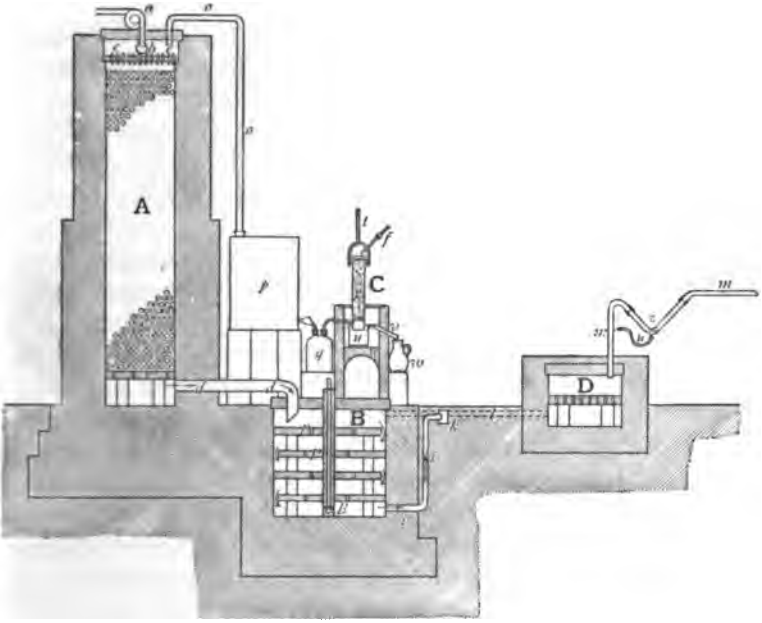

FIG. 53.

whilst the now quite innocuous liquor passes away by the pipe *i*.

The bromine vapour and excess of chlorine pass out from the top of the tower by the pipe *o*, through the condenser *p*, where most of the bromine condenses, the last traces of the bromine and chlorine being removed by the vessel C, which contains iron filings kept moist by a small stream of water.

The bromine thus obtained is purified by re-distillation, the small quantities of chlorine present being removed by the addition of potassium, or ferrous bromide, or by collecting separately the more volatile portions of the distillate, which contain all the chlorine in the form of chloride of bromine.

The manufacture of bromine was commenced at Stassfurt in 1865, in which year the quantity obtained only amounted to 25 cwt.; in 1885 the amount had risen to 260 tons, and has considerably increased since that time, whilst the quantity manufactured in America during 1885 was estimated at 120 tons, and in 1902 at 230 tons.

116 *Properties.*—Bromine is a heavy mobile liquid, so dark as to be opaque except in thin layers. It is the only liquid element at the ordinary temperature except mercury. Its specific gravity at 0° is 3·1883: it freezes at −7° to a dark brown solid, evaporates quickly in the air, boils at 59° (Thorpe), and crystallises from carbon bisulphide at −90° in slender dark carmine-red prisms. Bromine possesses a very strong, unpleasant smell; the vapours when inhaled produce great irritation, and affect the eyes very painfully. When swallowed it acts as an irritant poison, and when dropped on the skin it produces a corrosive sore which is very difficult to heal.

In its general properties, as well as in those of its compounds, bromine closely resembles chlorine, although they are not so strongly marked. Thus it bleaches organic colouring matters, but much less quickly than chlorine, and it combines directly with metals to form bromides, though its action is less energetic than that of chlorine. It does not combine at all at ordinary temperatures with metallic sodium; indeed these two substances may be heated together to 200° before any perceptible action commences, whereas bromine and potassium cannot be brought together without combination occurring, sometimes with almost explosive violence.[1] The addition, however, of a drop of water to bromine and clear sodium sets up a lively reaction. If

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[1] Merz und Weith, *Ber.*, 1873, **6**, 1518.

brought into contact with free bromine, starch-paste is coloured orange-yellow. The vapour density of bromine at temperatures slightly above its boiling-point is somewhat higher than the normal—namely, 5·8691 (air = 1), but at 228° the density is 5·5247, showing that at that temperature the bromine molecules contain 2 atoms.[1] Moreover, if bromine vapour be mixed with 10 volumes of air, its vapour density, calculated from that of the mixture, corresponds to the formula Br_2 even at the ordinary temperature.[2] At about 1,570° the observed density is about $\frac{2}{3}$ of that at 228°, so that, as in the case of chlorine, the molecules Br_2 are at this temperature partially dissociated into molecules consisting of simple atoms.[3]

Bromine is largely employed in the colour industry and also in medicine, whilst smaller quantities are used in analytical and synthetical chemistry, and as a disinfectant. To employ it for the latter purpose, advantage is taken of the fact that the siliceous earth known as "kieselguhr" absorbs as much as 75 per cent. of its weight of bromine, and still retains its solid form; the product is sold under the name of "bromum solidificatum."

117 *Bromine and Water.*—A definite crystalline compound of bromine and water is obtained by exposing a mixture of the two substances to a temperature near the freezing-point. This hydrate consists of $Br_2 + 10H_2O$, and undergoes decomposition into bromine and water at 15°. The analysis of the compound gave the following results:—

	Calculated.		Found (Löwig).
Bromine	79·36	47·00	45·5
Water	89·40	53·00	54·5
	168·76	100·00	100·0

From the dissociation pressure, Roozeboom[4] believes that it has the composition $Br_2 + 8H_2O$.

The solubility of bromine in water between the temperatures of 0° and 50° is shown in the following table:[5]—

	0°	10°·34	19°·96	30°·17	40°·03	49°·85
Parts of water dissolve 1 part of Bromine	24	26·74	27·94	29·10	29·02	28·39

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[1] Jahn, *Ber.*, 1882, **15**, 1238. [2] Langer and V. Meyer, *Ber.*, 1882, **15**, 2773.

[3] V. Meyer and Züblin, *Ber.*, 1880, **13**, 405; Crafts, *Compt. Rend.*, 1880, **90**, 183; Perman and Atkinson, *Zeit. physikal. Chem.*, 1900, **33**, 215.

[4] *Rec. Trav. Chim.*, 1885, **3**, 73. [5] Winkler, *Chem. Zeit.*, 1899, **23**, 687.

The solution of bromine in water has an orange-red colour; it soon loses bromine in contact with the air, and bleaches organic colouring matter. Bromine water is permanent in the dark, but on exposure to sunlight it becomes acid from the formation of hydrobromic acid and evolution of oxygen. Bromine also dissolves readily in chloroform, carbon bisulphide, alcohol, ether, and acetic acid.

The atomic weight of bromine has been determined by Marignac and by Stas; the latter obtained as a mean of a large number of experiments 79·36 as the atomic weight of bromine when that of oxygen is 15·88.

BROMINE AND HYDROGEN.

HYDROBROMIC ACID. $HBr = 80·36$ ($H = 1$).

118 Bromine, like chlorine, forms only one compound with hydrogen, containing one atom of bromine and one of hydrogen, but, unlike chlorine, these two bodies do not unite to form hydrobromic acid when brought together in sunlight. If, however, hydrogen and the vapour of bromine are passed through a red-hot tube containing finely-divided metallic platinum or pieces of charcoal,[1] combination occurs between equal volumes of bromine and hydrogen with formation of hydrobromic acid gas. The combination of these two bodies may be easily shown by passing hydrogen over bromine and lighting the escaping gas, when dense fumes of hydrobromic acid will be noticed.

Preparation.—Hydrobromic acid gas cannot well be prepared by the action of the ordinary acids on the bromides as in the case of hydrochloric acid, owing to the facility with which hydrobromic acid is oxidised, with formation of free bromine. If, however, phosphoric acid be used, pure hydrobromic acid is obtained.

Sulphuric acid of sp. gr. 1·41 liberates hydrobromic acid from potassium bromide without simultaneous formation of bromine, and in this manner a dilute solution of the acid may be obtained, which may be concentrated by distillation.[2]

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[1] Merz and Holzman, *Ber.*, 1889, **22**, 867.

[2] Feit and Kubierschky, *J. Pharm.*, 1891 [5], **24**, 159.

One of the best methods of preparing hydrogen bromide is to bring bromine and phosphorus together in presence of a little water, when a violent action occurs, hydrobromic acid gas and phosphoric acid being formed:—

$$P+5Br+4H_2O=5HBr+H_3PO_4.$$

In order to prepare the gas a flask provided with a doubly-bored caoutchouc cork, Fig. 54, is made use of; through one of the holes a gas delivery-tube is fixed, whilst through the other a stoppered funnel-tube is passed. A mixture of one part by weight of amorphous phosphorus and two parts of water is introduced into the flask, and ten parts of bromine are allowed to fall drop by drop through the stoppered funnel-tube on to the mixture in the flask. As each drop falls in, a sudden evolution of gas occurs, accompanied in the first part of the operation by a flash of light, and as soon as a certain amount of hydrobromic acid has been formed the bromine dissolves quietly, and on gently warming the flask hydrobromic acid gas is given off. This is then allowed to pass through a U-tube containing amorphous phosphorus, to free it from any vapour of bromine, and may be collected in dry stoppered cylinders by displacement or over mercury.

FIG. 54.

A second method is to pass a current of hydrogen sulphide evolved from one of the continuous apparatus through a layer of bromine contained in a tall cylindrical vessel, and covered by a layer of water or hydrobromic acid, when the following reaction takes place:

$$Br_2 + H_2S = 2HBr + S.$$

The liberated sulphur partially combines with the excess of bromine, forming bromides of sulphur. The gas evolved is washed by passing through a solution of potassium bromide in hydrobromic acid containing a little amorphous phosphorus in suspension, and is thus obtained free from bromine and sulphuretted hydrogen; with this method the evolution of the gas can be regulated very exactly.[1]

A third method is to pass a mixture of hydrogen and bromine vapour through a tube in which a platinum spiral is heated to bright redness. For this purpose a glass tube about 18 cm. in length and 15 mm. in width is fitted at each end with a cork carrying a small tube and a piece of stout copper wire; the ends of the stout wires are joined within the tube by a platinum spiral 1 in. in length, which is maintained at a bright red heat by means of an electric current; a stream of hydrogen is then bubbled through bromine heated to 60° and passed through the wide tube, the small tube being plugged with glass wool to prevent possible explosions. So long as the hydrogen is in slight excess, the hydrogen bromide is quite free from bromine, and the presence of a small quantity of hydrogen is of no importance for most purposes, especially when the aqueous solution of the acid is required.[2]

To prepare a solution of hydrobromic acid, the gas made by any of the methods named may be passed into water. This is best done by leading the delivery tube from the apparatus through a cork fitting in the tubulus of a retort placed in the position shown in Fig. 55; the neck of the retort dips under water, and the retort itself serves as a safety tube in case the gas should be so quickly absorbed that the liquid is forced back, as then the solution is not sucked back into the generating apparatus, but rushes into the bulb of the retort.

A very convenient method of preparing the aqueous solution direct is as follows:—350 c.c. of bromine are placed in a flask and covered with 2 litres of water; sulphur dioxide gas (best obtained from the liquid sulphur dioxide now sold in siphons) is then led into the water about 5—10 mm. above the

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[1] Recoura, *Compt. Rend.*, 1890, **110**, 784.

[2] Newth, *Chem. News*, 1891, ii. 215.

surface of the bromine until the whole is transformed into a pale yellow homogeneous liquid.

$$SO_2 + Br_2 + 2H_2O = 2HBr + H_2SO_4.$$

On distillation the hydrobromic acid solution passes over, leaving behind the sulphuric acid also formed. The distillate is purified by re-distilling over barium bromide to remove the last traces of sulphuric acid.[1] The acid thus obtained is free from arsenic, which is usually not the case when phosphorus has been employed in its preparation.

FIG. 55.

119 *Properties.*—Hydrobromic acid is a colourless gas, having a strong irritating smell, with an acid taste and reaction. It fumes strongly in the air, and on exposure to a temperature of −73° it condenses to a colourless liquid, and afterwards freezes at −87° to a colourless ice-like solid.[2]

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[1] Scott, *Journ. Chem. Soc.*, 1900, 648.
[2] Faraday, *Phil. Trans.*, 1845, p. 155.

Like hydrogen chloride, hydrogen bromide is decomposed by sunlight in presence of oxygen and moisture, with liberation of bromine, but the dry mixture of the gases is unaffected.[1]

Pure aqueous hydrobromic acid is colourless, and remains so even when exposed to air; it fumes when saturated at 0°, and then possesses a specific gravity of 1·78, its composition corresponding to the formula HBr, H_2O. The weak aqueous acid becomes stronger, and the concentrated acid weaker, on distillation, until an acid containing from 47·38 to 47·86 per cent. of HBr distils over under pressures varying from 752 to 762 mm. When the pressure under which the distillation occurs varies, the composition of the constant acid changes as that of hydrochloric acid does, and if a stream of dry air be passed through the aqueous acid a point is reached, different for each temperature, at which the acid no longer undergoes change. Thus the acid which evaporates unchanged in air at 100° contains 49·35 per cent. of HBr, whilst that obtained at 16° contains 51·65 per cent. of HBr.

The variation of the specific gravity of the aqueous acid with the percentage of hydrobromic acid dissolved has been determined by Topsöe,[2] as also by C. R. A. Wright,[3] who obtained the following numbers;—

Per Cent. HBr.	Spec. Grav. at 15°.
10·4	1·080
23·5	1·190
30·0	1·248
40·8	1·385
48·5	1·475
49·8	1·515

At low temperatures two crystalline hydrates of hydrobromic acid, HBr, H_2O and HBr, $2H_2O$ have been obtained,[4] and according to Pickering[5] the hydrates HBr, $3H_2O$ and HBr, $4H_2O$ exist at very low temperatures.

The composition of this gas is analogous to that of hydrochloric acid, and can be ascertained in a similar way by bringing a given volume of the dry gas in contact with sodium amalgam, when sodium bromide is formed and hydrogen liberated, the

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[1] Richardson, *Journ. Chem. Soc.*, 1887, 804.

[2] *Ber.*, 1870, **3**, 404.

[3] *Chem. News*, 1871, **23**, 242.

[4] Bakhuis Roozeboom, *Rec. Trav. Chim.*, 1886, **4**, 108; 1886, **5**, 363.

[5] *Phil Mag.*, 1893 [5], **36**, 111.

volume of which is found to be exactly half that of the original hydrobromic acid gas.

120 *The Bromides.*—These compounds are formed in a similar manner to the corresponding chlorides. They possess an analogous composition with these, and exhibit similar properties. Bromine unites with nearly all the metals, forming bromides, which are also produced by the action of metals on hydrobromic acid, or by the action of bromine vapour on the metallic oxides, oxygen being liberated.

The metallic bromides are nearly all soluble in water, the most insoluble being silver bromide, AgBr, mercurous bromide, HgBr, and lead bromide, $PbBr_2$, which latter is slightly soluble. All the bromides are solid at the ordinary temperature, but when heated they fuse and volatilise, some undergoing decomposition, others remaining unchanged. They are, however, all decomposed by chlorine, either in the cold or upon heating, a metallic chloride being formed and bromine liberated; they are also decomposed by sulphuric and nitric acids, with evolution of hydrobromic acid, which again is partly oxidised, bromine being set free.

Detection and Estimation of Bromine.—Bromine when in the free state may be recognised by the red colour of its vapour, by its exceedingly disagreeable odour, and by imparting to starch paste an orange-yellow colour. When present in small quantities it may be detected by shaking up with chloroform or ether, which dissolves it, and acquires thereby a red or brownish colour.

Bromine in the state of a soluble bromide may be detected by giving with silver nitrate a yellowish-white precipitate of silver bromide, which is insoluble in nitric acid, and dissolves only with difficulty in ammonia, but readily in cyanide of potassium. Also by giving with nitrate (but not chloride) of palladium a reddish-brown precipitate of the bromide; by its tinging carbon bisulphide yellow in presence of hydrochloric acid and a drop of sodium hypochlorite; and by the liberation of bromine on heating with sulphuric acid, with sulphuric acid and manganese dioxide, or with sulphuric acid and potassium bichromate.

When the bromine is present as a soluble bromide it is usually *estimated* by precipitation as bromide of silver, which contains 42·42 per cent. of bromine. In presence of chlorine the two elements are precipitated together by nitrate of silver; the precipitate is then fused and weighed. A portion of it is next ignited in a current of chlorine, when the whole of the bromine is expelled, the residue of silver chloride weighed, and from the weight thus obtained and that of the mixed silver salts the quantities of chlorine and bromine are calculated. For every 79·36 parts of bromine expelled, 35·18 parts of chlorine have been substituted; or, if a difference of 44·18 is observed, 79·36 parts of bromine must have been present. Hence, for any other difference the weight of bromine is found by multiplying that difference by $\frac{79\cdot36}{44\cdot18} = 1\cdot796$.

CHLORINE AND BROMINE.

121 *Bromine Monochloride*, BrCl.—When chlorine gas is passed into liquid bromine cooled below 10° it is largely absorbed, a reddish-brown volatile mobile compound of the two elements being formed.[1] It dissolves in water yielding a yellow solution, from which, on cooling below 0°, a crystalline hydrate $BrCl + 10H_2O$ separates out, which melts at + 7°. This is possibly simply a mixture of chlorine and bromine hydrates.

IODINE. $I = 125\cdot90$ (H = 1)
$= 126\cdot85$ (O = 16).

122 Iodine was discovered in 1812 by Courtois,[2] of Paris, in the mother-liquors of the soda salts which are prepared from kelp or burnt seaweed. It was afterwards examined by Davy,[3] and much more completely by Gay-Lussac.[4] Iodine derives its name from ἰοειδής, violet-coloured, owing to the peculiar colour of its vapour, by means of which it was first discovered.

Like chlorine and bromine, iodine does not occur in the free state in nature, but is found combined with metals to form iodides, which occur in small quantities, but widely diffused, both in the organic and inorganic kingdoms, having been detected in sea-water, in sea-plants and animals, and in many mineral springs. The quantity of iodine present in sea-water is extremely small, but certain plants and even animals have

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[1] Balard, *Ann. Chim. Phys.*, 1826 [2], **32**, 337; Bornemann, *Annalen*, 1877, **189**, 183.

[2] Courtois, Clement, and Desórmes, *Ann. Chim.*, 1812, **88**, 304.

[3] *Phil. Trans.*, 1814, **2**, 74 and 487.

[4] *Ann. Chim.*, 1813, **88**, 311, 319, and 1814, **91**, 5.

the power of absorbing and storing up the iodine. The ash of the deep-seaweed (*Fucus palmatus* especially) contains more iodine than that which grows in shallow water, and it is from the weed collected on exposed and rocky coasts, as the north and west coasts of Ireland, Scotland, and France, that a portion of the iodine of commerce is obtained. Of late years, however, the quantity manufactured from kelp has considerably decreased, owing to the discovery of iodine in the crude Chili saltpetre or Caliche, $NaNO_3$, from the mother-liquors of which it is now chiefly obtained; it is likewise found in combination with silver in a Mexican silver ore, in some specimens of South American lead ore, in certain dolomites, and in small quantities in almost every deposit of rock-salt. Iodine has also been found in coal, and it has been detected in some few land and fresh-water plants, and in many sea animals, as in sponges and oysters, and also in cod-liver oil and in the thyroid gland.

123 *Preparation from Seaweed.*—The stormy months of the spring are those in which the deep-sea tangle is thrown up on the north coasts of France and Ireland and the western coasts of Scotland. The inhabitants collect the weed, allow it to dry during the summer, and then burn it in large heaps. The ash thus obtained is termed *kelp* in Scotland, and *varec* in Normandy; it contains from 0·1 to 0·3 per cent. of iodine. When the seaweed is completely burnt, and when the ash is fused, a considerable fraction of the iodine is lost from volatilisation; hence it is preferable to carbonise the weed in closed retorts, the whole of the iodine remaining in the ash, whilst the tar and ammoniacal liquor are also recovered; the carbon remaining after the lixiviation of the ash resembles animal charcoal, and is used as a disinfectant.

In the most recent process for obtaining the iodine from seaweed the latter is directly lixiviated without previous carbonisation, the residual apparently unaltered plants being converted into *algin*, a substance which resembles gelatin and is employed as a substitute for bladder skins, &c. On lixiviating systematically either the kelp or the carbonised weed, a concentrated solution of the alkali carbonates, chlorides, sulphates, and a small quantity of sulphites and sulphides, together with the iodides and bromides of the alkali metals, is obtained, and from this solution the carbonates, chlorides, and sulphates are allowed to crystallise, leaving the bromides and the iodides in the mother-liquor. This liquor is then treated in several ways in order to obtain the iodine.

(1) An excess of sulphuric acid is added to the liquor, when the sulphides and sulphites which it contains are decomposed and the iodine and bromine liberated as hydriodic and hydrobromic acid. In this process the liquor, after any separated crystals of sodium sulphate which may have formed have been taken out, is placed in iron boilers, Fig. 56, surrounded with brickwork, each gently heated by a separate fire to a temperature of 60°, and fitted with leaden hoods, which can be lifted off by means of a chain and winch. Each cover is fitted with a leaden pipe (*a*), and this is connected with a series of glass or earthenware condensers, termed *udells,* fitting one into the other. After the introduction of the liquor, the covers are luted on with clay, the pipes (*a*) fixed in their receptacles and connected with the condensers. Manganese dioxide is then thrown little by little into the still through the hole (*b*), which can be closed by a stopper. The iodine thus liberated condenses in the receivers,[1] and the accompanying water escapes through a tubulus at the bottom of each receiver and runs away along the channel (*c*). When no

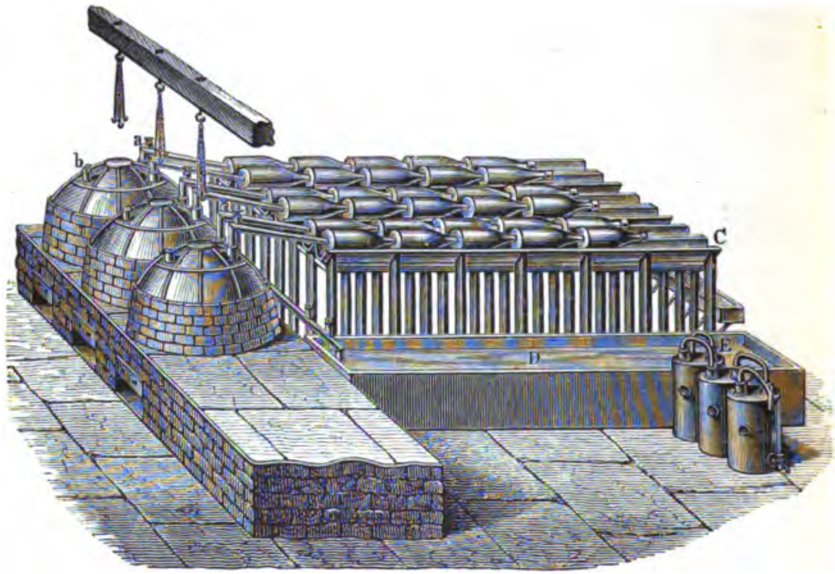

Fig. 56.

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[1] One ton of kelp usually yields 12 lbs. of iodine.

more iodine distils over, the leaden pipes are dismounted, and the stills are connected with a second receiver (D). More manganese dioxide is then added, and the bromine, which hitherto has not been liberated, is now disengaged and collects in (D) and in the Woulff's bottles (E).

The decomposition occurring during the formation of the iodine is represented by the following equation :—

$$2NaI + 3H_2SO_4 + MnO_2 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$$

The iodine thus obtained may then be partially purified by resublimation, but even then invariably contains traces of chloride, bromide, and cyanide of iodine.

(2) The iodine contained in the liquors, after separation of the crystallisable alkali salts, may also be liberated by the addition of sulphuric acid containing a considerable quantity of nitric acid. The acidified liquor is then agitated with the most volatile portion of petroleum (petroleum-naphtha, kerosine), which dissolves the iodine. The petroleum solution of iodine is next drawn off from the aqueous liquor and shaken up with an aqueous solution of caustic soda, whereby the iodine is withdrawn from the hydrocarbon and converted into iodide and iodate of sodium. The iodine is then liberated from these salts by the addition of hydrochloric acid, thus :—

$$5NaI + NaIO_3 + 6HCl = 6NaCl + 3H_2O + 3I_2.$$

(3) In France the mother-liquor is treated with a slight excess of sulphuric acid, filtered from sulphur, diluted to 40° Tw., and saturated with chlorine, care being taken to avoid adding an excess of the latter, which would cause loss owing to the formation of chloride of iodine. The iodine separates out in the solid form and is filtered off, dried, and resublimed.

124 *Preparation from Caliche.*—The crude Chili saltpetre, known as Caliche, now forms the chief source of iodine ; to obtain the iodine the last mother-liquor obtained in the preparation of the sodium nitrate, which contains about 20 per cent. of sodium iodate, is treated with a solution of sodium bisulphite ; the iodine separates out in the solid form, and is filtered off and purified by resublimation, the vapours being condensed in a series of udells similar to those shown in Fig. 56.

In order to purify the commercial iodine it is washed with a small quantity of water, dried on porous plates, and resublimed.

According to Stas,[1] the only mode of obtaining chemically-pure iodine (free from every trace of chlorine and bromine) is to dissolve the commercial resublimed substance in iodide of potassium solution, and then to precipitate the iodine by water. The precipitate is well washed with water and then distilled with steam, the solid iodine in the distillate collected and dried *in vacuo* over solid nitrate of calcium, which is frequently changed, and distilled afterwards over solid caustic baryta to remove the last traces of water and of hydriodic acid.

Meineke[2] recommends heating commercial iodine with a solution of calcium chloride of sp. gr. 1·35 containing a little potassium iodide and a few drops of hydrochloric acid, until the iodine has fused; after cooling, the cake of iodine is washed, dried, and twice resublimed, a little barium oxide being added the first time. Lean and Whatmough[3] prepare the pure element by heating purified cuprous iodide to 240° in a current of air, previously dried by passing through concentrated sulphuric acid, whilst Ladenburg[4] first converts potassium iodide into silver iodide by precipitation with silver nitrate, the precipitate being washed with dilute ammonia to free it from silver chloride; the silver iodide is then reduced with zinc and dilute sulphuric acid, the iodine precipitated with nitrous acid, distilled with steam, and dried over calcium chloride.

125 *Properties.*—Iodine is a bright, shining, crystalline, blackish-grey solid, which is usually opaque, but may be obtained in transparent films by deposition on glass surfaces at a temperature of about $-180°$.[5] The crystals when large possess almost a metallic lustre; it crystallises by sublimation in the rhombic system, in the form of prisms or pyramids (Fig. 57). Finer crystals are obtained from solution, either by exposing to the air a solution of iodine in ether, or allowing an aqueous solution of hydriodic acid to stand. The crystals thus obtained have the ratio of their axes represented by the numbers 4 : 3 : 2. The crystal represented in Fig. 57 *a* was obtained by Marignac from solution in hydriodic acid.

Iodine is a heavy substance, having a specific gravity of 4·948 at 17°, melting at 114°·2 and solidifying at 113°·6 according to Stas, whilst Ladenburg with iodine obtained by his method (*v.*

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[1] *Recherches*, p. 136.

[2] *Chem. Zeit.*, 1892, 1219, 1230.

[3] *Journ. Chem. Soc.*, 1900, 148.

[4] *Ber.*, 1902, **35**, 1256.

[5] Dewar, *Proc. Chem. Soc.*, 1898, 241.

ante) found a sp. gr. of 4·933 at 4°/4° and a melting-point of 116·1°. It boils at 184°·35 under 760 mm. pressure (Ramsay and Young[1]), 183°·05 corr. (Ladenburg), giving rise to a vapour which, seen by transmitted white light, possesses when chemically pure a splendid deep blue colour, but when mixed with air a reddish-violet colour (Stas). The specific gravity of iodine vapour was found by Deville and Troost to be 8·72 (air = 1), which corresponds to the density, 125·9, proving that the molecular weight at this temperature is 125·90 × 2 = 251·80 and that the molecular formula is I_2. When iodine vapour is heated above 700° its specific gravity begins to diminish until at 1,700° it becomes constant, and is half that at 700°, the vapour consisting entirely of monatomic molecules.[2] At the ordinary temperature it volatilises slowly, shining crystals being deposited on the sides of a bottle on the bottom of which a little iodine has been placed. It is a bad conductor of electricity, and possesses a peculiar smell less penetrating than, though similar to, that of chlorine and bromine. The specific heat of solid iodine is, according to the experiments of Regnault, 0·05412, and that of the liquid 0·10882. The latent heat of fluidity of iodine is 11·7 thermal units, and its heat of vaporisation 23·95 thermal units.

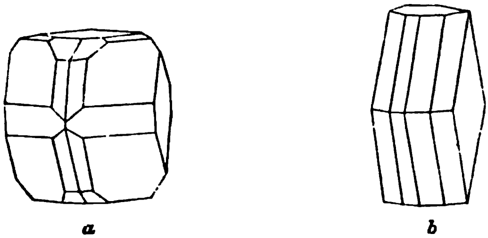

FIG. 57.

When an electric discharge is passed through a heated Geissler's vacuum-tube containing a trace of iodine vapour, a spectrum of bright lines is obtained, characteristic of this element.[3] This emission spectrum, however, does not correspond with the characteristic absorption-spectrum of iodine, so care-

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[1] Ramsay and Young, *Journ. Chem. Soc.*, 1886, 453.

[2] V. Meyer, *Ber.*, 1880, **13**, 394, 1010, 1103; V. Meyer and Biltz, *Ber.*, 1889, **22**, 725; Meier and Crafts, *Compt. Rend.*, 1880, **90**, 690; 1881, **92**, 39.

[3] Plücker and Hittorf, *Phil. Trans.*, 1865, 28.

fully mapped by Thalén,[1] and seen when white light is passed through iodine vapour. Salét[2] has shown that when an electric current of feeble tension is passed through a Geissler's tube containing iodine, another set of bright bands is obtained, which are identical in position with the dark bands of Thalén's absorption-spectrum, each bright band being replaced by a black band when the vapour is illuminated from behind.

126 In its chemical properties iodine resembles chlorine and bromine; the two latter elements have the power of displacing iodine from its combination with metals (or electro-positive elements), thus:—

$$2KI + Cl_2 = 2KCl + I_2.$$

The compounds of iodine with oxygen (or with electro-negative elements) are, on the other hand, more stable than those of the other two elements. Thus iodine expels chlorine from the chlorates with formation of iodate and free chlorine:—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

These differences are explained when we examine the amount of heat evolved by the several decompositions in question. This heat may be taken as an indication of the relative affinity or power of combination which the elements exhibit towards one another. Thus the heat evolved on the combination of chlorine, bromine, and iodine with hydrogen, or the *heat modulus* of the reactions according to Julius Thomsen's experiments,[3] is:—

$H + Cl$	21836	heat units
$H + Br$	8337	„
$H + I$	−6060	„

When these same elements unite with oxygen and hydrogen to form the oxyacids ($HClO_3$, $HBrO_3$, HIO_3) the heat evolved is as follows:—

$Cl + 3\,O + H$ . . .	23761	heat units
$Br + 3\,O + H$ . . .	5344	„
$I + 3\,O + H$ . . .	43211	„

Hence we see that, as regards affinity for oxygen, chlorine stands nearly midway between bromine and iodine, for $\frac{43211 + 5344}{2} = 24277.$

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[1] *Kon Svenska Acad. Handb.*, 1869.
[2] *Phil. Mag.*, 1872 [4], **44**, 156.
[3] *Journ. Chem. Soc.*, 1873, 1188.

Iodine is very sparingly soluble in water, 1 part dissolving in 3,750 parts of water at 15° and in 2,200 at 30°. It dissolves readily in a solution of potassium iodide, forming a brown solution, in which, however, the iodine is probably not present as such, but as the unstable potassium triiodide KI_3. It also dissolves readily in a large number of other solvents, in some of which, such as chloroform, carbon bisulphide, and liquid hydrocarbons, it gives rise to violet solutions, whilst with others, such as alcohol, ether, organic acids and esters, and pyridine, it yields yellow or brown solutions. The cause of the difference of colour of the various solutions has not yet been ascertained with certainty, but it seems most probable that in the violet solutions iodine is present as such, whilst the brown solutions contain an unstable compound of iodine with the solvent. The first-named class of solutions when concentrated are black and opaque; in the case of carbon bisulphide, such a solution is diathermanous, allowing the invisible heating rays of low refrangibility to pass, but not the visible rays.

The tincture of iodine of the Pharmacopœia contains ½ oz. iodine, ¼ oz. potassium iodide, and 1 pint of rectified spirit.

Although iodine, unlike chlorine and bromine, does not combine readily with hydrogen, it unites with many of the metals and non-metals with evolution of light and heat. Thus solid phosphorus, when brought into contact with iodine, first melts and then bursts into flame owing to the heat evolved in the act of combination: and powdered antimony takes fire when thrown into iodine vapour, antimony iodide being produced; whilst if the vapour of mercury be passed over heated iodine, immediate action occurs, the iodides of mercury being formed. When iodine is brought into contact with water and filings of iron or zinc, a violent reaction occurs, colourless solutions of the respective iodides resulting. The action of iodine upon the alkali-metals is analogous to that of chlorine and bromine. Sodium and iodine can be heated together without any alteration, whilst if potassium be employed an explosive combination occurs.

Potash at once decolorises a solution of iodine, iodide and iodate of potassium being the final products, thus:—

$$3I_2 + 6KHO = 5KI + KIO_3 + 3H_2O.$$

When acted upon by strong nitric acid, iodine is completely oxidised to iodic acid, HIO_3.

The most characteristic property of free iodine is its power of forming a splendid blue colour with starch-paste. This is formed when starch granules are brought into contact with the vapour of iodine, or, better, when a solution of iodine is added to starch-paste. The blue colour disappears on warming the solution, but reappears on cooling, and its formation serves as a most delicate test for the presence of iodine.[1] In order to exhibit this property, a few grains of iodide of potassium may be dissolved in three or four litres of water placed in a large glass cylinder, and some clear, dilute, well-boiled starch-paste added. As the iodine is here combined with the metal, no coloration will be seen, but if a few drops of chlorine water be added, or, better, if a little of the air (containing free chlorine) from a bottle of chlorine water be poured on to the surface of the liquid, a blue film will be formed, which on stirring will impart a blue tint to the whole mass.

Iodine both free and in combination is largely used in medicine.

The atomic weight of iodine has been very accurately determined in several ways by Marignac and Stas, the mean value obtained from a large number of closely-agreeing experiments being 125·90 ($H = 1$), or 126·85 ($O = 16$). Ladenburg[2] has recently obtained the rather higher number 126·00 ($H = 1$) or 126·96 ($O = 16$).

IODINE AND HYDROGEN.

HYDRIODIC ACID. HYDROGEN IODIDE. $HI = 126·90$ ($H = 1$).

127 Iodine and hydrogen undergo partial combination when they are passed over finely-divided platinum heated to redness, or over charcoal at a bright red heat,[3] forming a strongly acid gas, having properties very similar to hydrochloric and hydrobromic acid.

Hydriodic acid can also be obtained by heating iodide of potassium with phosphoric, but not with sulphuric, acid; for when this latter acid is used, sulphur dioxide SO_2 and free iodine are formed at the same time, thus:—

$$3H_2SO_4 + 2KI = 2KHSO_4 + I_2 + SO_2 + 2H_2O.$$

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[1] Collin and Gaultier de Claubry, *Ann. Chim.* **90**, 87.

[2] *Ber.* 1902, **35**, 2275.

[3] Merz and Holzmann, *Ber.* 1889, **22**, 867.

On the other hand, hydriodic acid is easily prepared by allowing iodine and phosphorus to act on one another in presence of water, thus:—

$$P + 5I + 4H_2O = 5HI + H_3PO_4.$$

Preparation.—For this purpose 1 part by weight of red phosphorus and 15 parts of water are brought together in a tubulated retort or flask provided with a caoutchouc cork and gas delivery tube, and to these 20 parts of iodine are gradually added, the contents of the flask during this operation being kept cool by immersing the flask in cold water. When all the iodine has been added, and as soon as no further evolution of gas can be noticed, the flask may be gently warmed. The gas thus obtained may either be received in dry bottles filled with mercury in the mercurial trough, or it may be collected by displacement, as it is more than four times as heavy as air. To prepare aqueous hydriodic acid, the gas may be passed directly into water in the apparatus shown in Fig. 58.

If we possess a concentrated solution of hydriodic acid, the gas may be obtained in a still more simple manner. Two parts of iodine are dissolved in aqueous hydriodic acid of specific gravity 1·7, and this solution is allowed to fall, drop by drop, by means of a stoppered funnel-tube, into a flask containing red phosphorus covered with a thin layer of water. The evolution of gas occurs at first without any application of heat being necessary, but after a time the flask may be slightly warmed.

When hydriodic acid is prepared by the foregoing methods it frequently contains phosphuretted hydrogen; the formation of this impurity may, however, be avoided if the iodine is never allowed to come in contact with an excess of phosphorus. According to Lothar Meyer, this may be readily carried out as follows:—100 parts of iodine moistened with ten parts of water are placed in a tubulated retort, the neck of which is inclined upwards; a thin paste of 5 parts of red phosphorus and 10 parts of water is then allowed gradually to drop in through the tubulus of the retort. For this purpose a dropping funnel is employed, which, in place of a stopcock, is furnished with a glass rod, ground at the lower end to fit into the funnel tube; by raising the rod, small quantities of the paste are allowed to pass into the retort. The first few drops must be added cautiously, waiting each time for the reaction to moderate, as otherwise an explosion may occur; after a short time, however, larger quantities may be added at once, and the mixture may be completed in a quarter of an hour. The iodine carried over mechanically settles for the most part in the neck of the retort, and may be removed completely in most cases by washing with a little water.[1] The collection of the gas or the preparation of the solution may be carried out in the manner already described.

Fig. 58.

128 *Properties.*—Hydriodic acid exists at the ordinary temperature and pressure as a colourless gas, having a strongly acid reaction and suffocating odour, and fuming strongly in the air. It can be condensed to a colourless liquid[2] by a pressure of four atmospheres at 0°, or by exposure, under the ordinary atmospheric pressure, to the low temperature of a bath of ether and solid carbonic acid, and if cooled to $-55°$ it freezes to a colourless ice-like solid mass.

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[1] *Ber.* 1887, **20**, 3381.

[2] Faraday, *Phil. Trans.* 1845, **1**, 170.

The specific gravity of the gas (air = 1) has been found to be 4·3737, or 62·94 (H = 1), thus closely corresponding to its theoretic density, 63·45.

Hydriodic acid gas is easily decomposed by heat into iodine and hydrogen, as is seen by the violet colour which appears when the gas is passed through a heated glass tube. A hot metallic wire plunged into the gas also causes an immediate decomposition, violet fumes of iodine making their appearance.

129 The aqueous acid is obtained by passing the gas into water, by which it is absorbed quickly and in large quantities, yielding, when kept cold by ice, a solution which is twice as heavy as water, having a specific gravity, according to De Luynes, of 1·99. A simple mode of preparing a dilute aqueous solution of hydriodic acid consists in passing a current of sulphuretted hydrogen gas through water in which finely-divided iodine is suspended, the reaction which occurs being as follows:—

$$H_2S + I_2 = 2HI + S.$$

On standing, the clear liquid may be poured off from the precipitated sulphur and boiled to expel any trace of sulphuretted hydrogen. It is found that the strongest acid which can in this way be prepared has a specific gravity of 1·56.

On distillation, aqueous hydriodic acid behaves like aqueous hydrochloric and hydrobromic acids, both the strong and weak aqueous acid yielding on distillation in an atmosphere of hydrogen (to prevent oxidation and liberation of iodine) an acid of constant composition, boiling at 127° (under a pressure of 774 mm.) and containing 57·0 per cent. of hydriodic acid. If dry hydrogen be led through aqueous acids of varying strengths, each will attain the same constant composition at the same temperature; thus from 15° to 19° the constant acid contains 60·3 to 60·7 per cent. of HI. When the hydrogen is passed through the liquid at 100°, the percentage of hydriodic acid in the constant acid is 58·2,[1] and hence it is seen that no definite hydrate of the acid is obtained by boiling, as was formerly supposed. Aqueous hydriodic acid also rapidly undergoes oxidation with liberation of iodine when exposed to the air, the colourless solution becoming brown owing to the solubility of iodine in the acid. Gaseous hydrogen iodide is also decomposed by dry oxygen when the mixed gases are exposed to bright sunlight, and differs in this respect from

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[1] Roscoe, *Journ. Chem. Soc.* 1861, 160.

hydrogen chloride and bromide which are only decomposed by oxygen in presence of moisture.[1]

130 *The Iodides.*—The metallic iodides possess great analogy with the corresponding chlorides and bromides; they are all solid bodies, less fusible and volatile than the corresponding chlorides and bromides. Silver iodide, AgI, mercurous iodide, HgI, and mercuric iodide, HgI_2, are insoluble in water, and lead iodide, PbI_2, sparingly soluble, whilst the other metallic iodides dissolve readily in water. Most of the iodides are decomposed on heating, either the metal or an oxide being formed and iodine set free.

All the iodides, whether soluble or insoluble in water, are decomposed by chlorine and nitrous acid, the iodine being liberated. Some of the insoluble iodides possess a brilliant colour. Thus, on adding a solution of corrosive sublimate (mercuric chloride) to a soluble iodide, a salmon-coloured precipitate is thrown down, which rapidly changes to a brilliant scarlet one of mercuric iodide, HgI_2, soluble in excess of either reagent; a soluble lead salt, such as the nitrate or acetate, produces a bright yellow precipitate of lead iodide, PbI_2; silver nitrate gives a light yellow precipitate of silver iodide, AgI, insoluble in nitric acid and in ammonia. If a mixture of ferrous sulphate, $FeSO_4$, and copper sulphate, $CuSO_4$, be added to a solution of a soluble iodide, a greenish-white precipitate of cuprous iodide, CuI, is formed. This reaction depends upon the fact that ferrous sulphate is oxidised to ferric sulphate, $Fe_2(SO_4)_3$, whilst cuprous iodide is precipitated, thus :—

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + K_2SO_4 + Fe_2(SO_4)_3.$$

This reaction serves as a means of roughly separating iodine from a mixture containing chlorides and bromides.

The metallic iodides can be prepared by similar processes to those which yield the chlorides and bromides (p. 205).

131 *Detection and Estimation of Iodine.*—For the detection of iodine, the starch reaction, the violet-coloured vapours, and the above-mentioned coloured precipitates are sufficient.

To estimate iodine in the free state, a standard solution of sulphurous acid may be employed, and the point ascertained at which sufficient of this solution has been added to reduce all the iodine to hydriodic acid, thus :—

$$I_2 + 2H_2O + SO_2 = 2HI + H_2SO_4.$$

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[1] Richardson, *Journ. Chem. Soc.* 1887, 805.

The solution of sulphurous acid may be replaced by one of sodium thiosulphate, a substance which reacts with free iodine in the following manner:—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

For the quantitative determination of iodine in a soluble iodide and for the exact separation from chlorine or bromine, use may be made of the fact that palladium nitrate, $Pd(NO_3)_2$, produces with solutions of an iodide an insoluble precipitate of PdI_2, which on ignition yields metallic palladium. Iodine when in the form of an alkali iodide can be weighed also as iodide of silver, when neither chlorine nor bromine is present; 100 parts of silver iodide contain 54·128 parts of iodine. In the case of the insoluble iodides, it is best either to transform them into soluble iodide of sodium by fusing them with sodium carbonate or to digest them with zinc and dilute sulphuric acid, when hydriodic acid is liberated, thus:—

$$2AgI + Zn + H_2SO_4 = 2HI + 2Ag + ZnSO_4.$$

If it is required to determine chlorine, bromine, and iodine when mixed in solution together the following method may be employed:—

Field has shown[1] that chloride of silver is completely decomposed by digestion with bromide of potassium, the chlorine and bromine changing places; and that both bromide and chloride of silver are decomposed in like manner by iodide of potassium. Hence, if a solution containing chlorine, bromine, and iodine be divided into three equal parts, each portion precipitated by nitrate of silver, the first precipitate dried and weighed, the second digested with bromide of potassium, then dried and weighed, and the third digested with iodide of potassium, then dried and weighed, the relative quantities of the three elements may be determined from the following equations:—

$$x + y + z = w.$$

$$\frac{186{\cdot}48}{142{\cdot}30}x + y + z = w',$$

$$\frac{233{\cdot}02}{142{\cdot}30}x + \frac{233{\cdot}02}{186{\cdot}48}y + z = w'',$$

where w, w′, w″ are the weights of the three precipitates, and

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[1] *Journ. Chem. Soc.* 1858, 234.

x, y, and z the unknown quantities of chloride, bromide, and iodide of silver respectively.

The mixture of the three salts of silver may also be treated with a solution of potassium bichromate in sulphuric acid, which converts the chloride and bromide into the soluble sulphate, whilst the iodide is converted into the insoluble iodate. After dilution and filtration the iodate may be reduced and the silver in it determined, whilst the silver originally present as chloride and bromide may also be determined in the filtrate.[1]

IODINE COMPOUNDS WITH OTHER HALOGENS.

132 *Iodine Pentafluoride*, IF_5, is formed by passing fluorine over dry iodine. It forms a colourless liquid, which solidifies at 8° to a solid resembling camphor, boils at 97°, and undergoes decomposition at 400—500°, free iodine being formed. It is acted on by sulphur, arsenic, antimony, and carbon in the cold and by chlorine and bromine on warming, and is completely decomposed by water into iodic and hydrofluoric acids, and also by solutions of the alkalis. It attacks silica and many silicides and carbides, and when dropped into turpentine causes it to ignite.[2]

Iodine and Chlorine.—Two compounds of iodine and chlorine are known:—(1) Iodine monochloride, ICl. (2) Iodine trichloride, ICl_3. They are both obtained by the direct union of chlorine and iodine, the higher chloride being formed when the former element is in excess.

Iodine Monochloride, ICl, is prepared (1) by passing dry chlorine gas over dry iodine until the latter is completely liquefied; (2) according to Berzelius, by distilling 1 part of iodine with 4 parts of potassium chlorate, the chlorine evolved by the reaction combining with a portion of the iodine;[3] (3) by boiling iodine with strong aqua regia; after dilution with water the liquid is shaken up with ether in which the chloride of iodine dissolves and remains behind when the ether is evaporated.[4]

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[1] Macnair, *Proc. Chem. Soc.* 1893, 181.

[2] Moissan, *Compt. Rend.* 1902, **135**, 563.

[3] Thorpe and Perry, *Journ. Chem. Soc.* 1892, 925.

[4] Bunsen, *Annalen*, 1852, **84**, 1.

The product thus obtained is a reddish-brown oil, which, on standing, solidifies, forming long well-defined crystals melting at 24°·7; it boils at 101°·3 and has a sp. gr. at that temperature of 2·88196 (Thorpe). It smells like a mixture of chlorine and iodine, and bleaches indigo solution, but does not colour starch-paste blue.

A second modification, known as β-iodine monochloride, is obtained by heating the crude monochloride till it is free from trichloride, and then cooling to −10°. It melts at 13°·9.[1]

Iodine Trichloride, ICl_3, is obtained (1) by acting on iodine, gently heated, with a large excess of chlorine; (2) by treating iodic acid, HIO_3, with hydrochloric acid; (3) by heating iodine pentoxide, I_2O_5, with pentachloride of phosphorus, PCl_5.

This compound forms long lemon-coloured crystals and very readily undergoes dissociation. When heated in the air to 25° it decomposes, giving off chlorine gas, forming the monochloride; but when heated in an atmosphere of chlorine it only decomposes at a much higher temperature, which rises as the pressure of the chlorine is increased. Thus under a pressure of one atmosphere it decomposes at 67° into the monochloride and free chlorine, and these again unite on cooling to form a yellow sublimate of the trichloride.[2]

Both the chloride and trichloride dissolve in water, ether, and alcohol apparently without decomposition. When either of them is acted upon by a small quantity of an alkali, an iodate and chloride are formed and iodine is liberated,[3] potassium hypoiodite, KOI, being formed as an intermediate product—

$$6KHO + 5ClI = 5KCl + KIO_3 + 2I_2 + 3H_2O.$$

They are both very hygroscopic and give off irritating vapours.

The formation of both these compounds can be demonstrated by inverting a small cylinder containing chlorine and bringing its mouth in contact with that of another of the same size filled with hydriodic acid gas. Iodine is first liberated, which combines with the excess of chlorine, the yellow trichloride being deposited on the sides of the upper jar, in which chlorine is in large excess, whilst the brown monochloride, mixed with iodine, is formed in the lower jar.

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[1] Tanatar, *Journ. Russ. Chem. Soc.* 1893, **25**, 97.

[2] Brenken, *Ber.* 1875, **8**, 487.

[3] Philip, *Ber.* 1870, **3**, 4.

Iodine unites with bromine to form a solid, volatile, crystalline compound which is probably the monobromide, and also a dark liquid, possibly the tribromide. These bodies possess properties similar to those of the chlorides of iodine.

OXYGEN. $O = 15{\cdot}88$ $(H = 1)$.
$O = 16{\cdot}00$ $(H = 1{\cdot}008)$.

133 Of the elements which occur in our planet, oxygen is the most widely diffused, and is found in the largest quantity. The old crystalline rocks, which constitute the chief mass of the earth's crust, consist of silicates, or compounds of silicon and various metals with oxygen. These rocks contain from 44 to 48 per cent. of oxygen. Water likewise is a compound of oxygen and hydrogen, containing 88·81 per cent. of the former element. Oxygen also exists in the free state in the atmosphere, which contains about 21 per cent. of its volume of this gas. Although the absolute amount of free oxygen contained in the air is very great, yet the proportion which it bears to that in a state of combination in the solid earth and in the form of water is but very small.

It has already been mentioned, in the Historical Introduction, that the air was believed to be a simple or elementary substance until the investigations of Priestley, Rutherford, and Scheele[1] showed distinctly that it is a mixture of two different gases, only one of which is capable of supporting combustion and respiration. This constituent of the atmosphere is oxygen, discovered on the 1st of August, 1774, by Priestley, who, by heating "red precipitate" (mercuric oxide) by means of the sun's rays, decomposed it into oxygen and metallic mercury. The discovery of oxygen enabled Lavoisier to put forward the true theory of combustion, and to the body capable of supporting this combustion was given the name "oxygen" (ὀξύς sour, and γεννάω I produce), from the fact that the products of combustion are frequently of an acid nature.

134 *Preparation.*—(1) The simplest method of preparing oxygen is to heat mercuric oxide, HgO, in a small retort of hard

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[1] It appears that Scheele had prepared oxygen prior to the date of Priestley's discovery, but that these results were not published until after Priestley's experiments had been made known. See *Carl Wilhelm Scheele: Nachgelassene Briefe und Aufzeichnungen*, edited by A. E. Nordenskiöld (Stockholm, 1892).

glass. The oxide decomposes at a red-heat into metallic mercury and oxygen; 100 parts by weight yield 4·7 parts by weight of oxygen.

$$2\,HgO = 2Hg + O_2.$$

The apparatus in which this decomposition can be shown is seen in Fig. 59. Owing to the comparatively high price of oxide of mercury, this process is only used as a means of illustrating the decomposition.

(2) The best and most usual mode of preparing oxygen consists in heating potassium chlorate, commonly called chlorate of potash, $KClO_3$, this salt losing the whole (39·14 per cent. of its weight) of its oxygen, leaving potassium chloride.

Fig. 59.

The preparation and collection of the gas, according to this method, may be carried on in the apparatus shown in Fig. 60. The temperature has to be raised somewhat above the melting-point of the salt (372°) before the evolution of gas begins, and after a time the fused mass becomes thick owing to the formation of potassium perchlorate, $KClO_4$. The two reactions

$$(1)\ 2KClO_3 = 2KCl + 3O_2$$
$$(2)\ 4KClO_3 = 3KClO_4 + KCl$$

therefore proceed simultaneously at first, and the amount of perchlorate gradually increases, and this, when the temperature is further raised, itself decomposes into potassium chloride and oxygen,[1]

$$KClO_4 = KCl + 2O_2.$$

In addition the secondary reaction

$$(3)\ 4KClO_3 = 2K_2O + 2Cl_2 + 5O_2$$

appears to take place, but in the case of the potassium salt this only occurs to an exceedingly small extent: with the chlorates of less basic metals, such as those of silver and lead, however, the corresponding reaction occurs very largely.[2]

The gas can be obtained at a lower temperature by employing a mixture of potassium and sodium chlorates (Shenstone).

(3) In order to obtain the evolution of oxygen at a still lower temperature, a small quantity of manganese dioxide is generally mixed with the powdered chlorate; the oxygen then comes off at about 350° before the salt fuses, and thus the preparation of the gas is greatly facilitated. The manganese dioxide is found, mixed with potassium chloride, in the residue unaltered in composition.

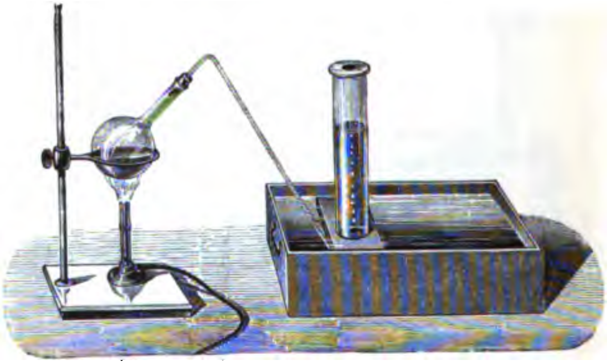

FIG. 60.

To prepare oxygen on a larger scale this mixture of potassium chlorate and manganese dioxide is heated in a thick copper vessel, provided with a wide tube connected with a wash-bottle containing caustic soda, for the purpose of absorbing

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[1] Frankland and Dingwall, *Journ. Chem. Soc.* 1887, 274; Teed, *ibid.* p. 283; Sodeau, *ibid.* 1902, 1066; Scobai, *Zeit. physikal. Chem.* 1903, **44**, 319.

[2] Sodeau, *Journ. Chem. Soc.* 1901, 247.

chlorine gas, which is always evolved in small quantity along with the oxygen. It not unfrequently happens that the commercial black oxide of manganese may be accidentally mixed or adulterated with carbon (pounded coal), and this impure material, when mixed with potassium chlorate and heated, ignites, giving rise to even fatal explosions. Hence care should be taken to try any new or doubtful sample on a small scale beforehand by heating it with potassium chlorate in a test-tube.

In addition to manganese dioxide, many other substances facilitate the evolution of oxygen from potassium chlorate, the action being most pronounced in the case of the oxides of copper, iron, nickel, and cobalt, and of platinum black (which always contains oxygen); many acidic oxides also accelerate the action although to a smaller extent, and these last also bring about a large increase in the amount of free chlorine evolved with the oxygen. The exact manner in which these substances act is not yet fully known, although many investigations have been made on the subject.[1]

The substances mentioned above, as lowering the temperature of decomposition to the greatest extent, are all known to be capable of existing in a higher state of oxidation, and it appears probable that in these cases an alternate formation of the higher oxide and decomposition of the latter into oxygen and the original oxide takes place. McLeod[2] has shown by means of the microscope that the particles of manganese dioxide are broken up and attacked during the reaction, and has further found that potassium permanganate is formed in small quantity. He, therefore, suggested that the primary reaction is as follows:—

$$2KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2,$$

the permanganate being then broken up by the combined action of heat and of the chlorine simultaneously produced with formation of potassium chloride and oxygen, and reformation of manganese dioxide. It has, however, been shown by Sodeau[3] that this cannot represent the chief reaction, although it probably takes place to a small extent, and may form the source of the chlorine evolved.

In the case of the acidic oxides it seems most likely that these enable the decomposition of potassium chlorate, according to

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[1] For a list of papers relating to the matter, see Sodeau, *Journ. Chem. Soc.* 1902, 1067.

[2] *Journ. Chem. Soc.* 1889, 184.

[3] *Journ. Chem. Soc.* 1902, 1066.

equation (3) on p. 236, to take place at a lower temperature, the acidic oxide uniting with the K_2O to form a salt, as with these oxides a much larger quantity of free chlorine is evolved.

(4) Many other salts behave like potassium chlorate in yielding oxygen on heating; among these are the hypochlorites, chlorites, perchlorates, bromates, and perbromates, as well as the iodates, periodates, nitrates, nitrites, and permanganates; but these compounds are not usually employed for this purpose.

(5) Several oxides, such as manganese dioxide, MnO_2, lead dioxide, PbO_2, barium dioxide, BaO_2, chromium trioxide, CrO_3, lose a portion of their oxygen when strongly heated, and all these may, therefore, be used for preparing oxygen. In order to obtain oxygen by heating the first-named oxide, the substance is placed in a strong iron bottle which can be heated in a furnace to bright redness (Fig. 61). The pure manganese dioxide loses one-third of its oxygen (12·4 per cent.), being converted into the brown oxide, Mn_3O_4, thus:—

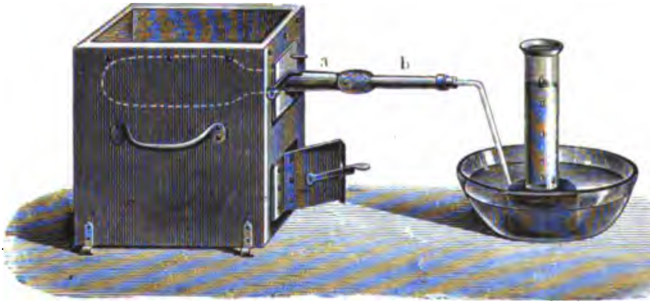

FIG. 61.

$$3MnO_2 = Mn_3O_4 + O_2.$$

(6) By heating manganese dioxide in a glass flask with sulphuric acid, one-half of its oxygen is given off, and manganous sulphate, $MnSO_4$, is formed—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

(7) Chromium trioxide can also be employed for the preparation of oxygen, but it is not necessary to obtain this substance in the pure state, for if potassium bichromate, $K_2Cr_2O_7$, be heated with sulphuric acid, chromium trioxide is formed, thus:—

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + 2CrO_3 + H_2O.$$

The chromium trioxide is then further decomposed by the action of sulphuric acid with the formation of chromium sulphate, a decomposition which is rendered visible by the change of colour from the original red to a deep green, thus:—

$$4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2.$$

(8) A convenient method for preparing pure oxygen without the necessity of heating, is by the action of a mixture of 150 grams of concentrated sulphuric acid with 1 litre of aqueous commercial hydrogen dioxide on solid potassium bichromate.[1] The latter must be in large crystals, and the liquid added gradually, otherwise the reaction is very violent. Kipp's apparatus (described under Sulphuretted Hydrogen) may be used for the preparation of the gas by this method, if a layer of small pieces of pumice is placed below the potassium bichromate in the middle bulb. The chromium trioxide first formed by the action of the sulphuric acid on the bichromate is decomposed by the hydrogen peroxide in presence of acid in the manner represented by the equation,

$$2CrO_3 + 3H_2O_2 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O + 3O_2.$$

(9) Oxygen can be obtained by the decomposition of bleaching powder (Mitscherlich, 1843; Fleitmann, 1865). For this preparation a clear concentrated solution of bleaching powder —which contains calcium hypochlorite, $CaCl_2O_2$—is placed in a flask, and a few drops of cobalt chloride solution added. An oxide of cobalt, which probably has the formula[2] CoO_2, is precipitated, and on heating the mixture to about 80° a rapid effervescence of oxygen occurs. The cobalt oxide formed is left unchanged after the operation, and may be employed again; it probably acts, like the manganese dioxide, by the formation of a higher oxide, which is again quickly reduced, the oxygen being liberated as a gas. Instead of a clear solution, a thick paste of bleaching powder may be used, with the addition of a little cobalt salt and a small quantity of paraffin oil to prevent the frothing which usually occurs. The best temperature for the evolution of the gas is from 70—80°:

$$CaCl_2O_2 = CaCl_2 + O_2.$$

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[1] Blau, *Monatsh.* 1892, **13**, 281; Erdmann and Bedford, *Ber.* 1904, **37**, 1184.

[2] Vortmann, quoted by McLeod, *British Ass.* 1892, 669.

The same decomposition and the replacement of chlorine for oxygen may be shown in a striking manner by passing chlorine gas, generated in a flask from manganese dioxide and hydrochloric acid, into a second flask, which contains boiling milk of lime to which a little cobalt nitrate solution has been added. Oxygen gas is then liberated in the second flask, and may be collected as usual. The following equation explains the replacement, and we see that two volumes of chlorine yield their equivalent, or one volume of oxygen:—

$$2Cl_2 + 2Ca(OH)_2 = 2CaCl_2 + 2H_2O + O_2.$$

(10) Oxygen can also be prepared by the decomposition of sulphuric acid. For this purpose a thin stream of sulphuric acid flows into a platinum retort heated to redness; the acid splits up into sulphur dioxide, water, and oxygen, yielding 15·68 per cent. of its weight of the gas, or in practice 55 grams of acid yield 6 litres of gas, thus:—

$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2.$$

The resulting sulphur dioxide and water can be absorbed, whilst the oxygen can be collected in a gas-holder.

135 In order to prepare oxygen cheaply on the large scale several other processes have been suggested. Amongst them the following is now widely used.

(11) When baryta, BaO, is gently heated to dull redness in the air, it takes up an additional atom of oxygen, forming the dioxide, BaO_2, but at a bright-red heat this parts with the additional atom of oxygen with the reproduction of baryta. By thus alternately varying the temperature, first leading air over the baryta contained in a porcelain tube, and then placing the tube in connection with a gas-holder and raising the temperature, and again repeating the process, a regular production of gas can be obtained from a small quantity of baryta.[1] This simple method somewhat modified is now carried out on a large scale according to the following process patented by the Brin Oxygen Company.[2]

Oxide of barium, prepared from the nitrate, is introduced in pieces about the size of walnuts into steel or cast-iron retorts.

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[1] Boussingault, *Ann. Chim. Phys.* 1852 [3], **35**.

[2] Pat. 157, Oct. 5, 1885.

These retorts, placed in a vertical position in a gas furnace, are heated to about 700°, and air, carefully purified from moisture and carbonic acid, then pumped through them under a pressure of about 15 lbs. on the square inch. The baryta absorbs the oxygen, becoming converted into peroxide, and as soon as this peroxidation has been carried as far as is economical the pump is reversed and the pressure in the retorts thus reduced. When the reduction of pressure has reached about 26—28 inches of mercury below the normal, the peroxide begins to give up its oxygen, which passes through the pump and is delivered to a gas-holder. A complete operation lasts about ten minutes, and nearly 140 operations can be conducted per diem. The oxygen is then compressed at 120 atmospheres in mild steel cylinders.[1]

Oxygen for technical purposes is also now obtained from liquid air, which is produced on the large scale by the Linde and Hampson processes (p. 108). As nitrogen boils at a lower temperature than oxygen, the liquid formed is much richer in the latter than the air from which it is obtained, and by suitable fractionation a gas containing 94 per cent. of oxygen may be obtained. For many purposes a gas containing 50 per cent. of oxygen is sufficient, and such a mixture is very readily produced from liquid air.

136 *Properties.*—Oxygen is a colourless, invisible, tasteless, inodorous gas, which is slightly heavier than air. The weight of 1 litre of the gas has been found by Morley,[2] as the result of a long series of determinations carried out with every conceivable precaution, to be 1·42900 under normal conditions at sea-level in the 45th degree of latitude, or 1·42945 grams for normal conditions of temperature and pressure at Paris, these numbers closely agreeing with the determinations of Rayleigh,[3] Leduc,[4] Thomsen,[5] and Guye and Mallet.[6] Compared with hydrogen the density of oxygen is 15·882; its molecular weight is therefore about 31·76, and molecular formula O_2. At −182° under diminished pressure the relative density remains the same (Dewar).

Oxygen was first liquefied by Cailletet and Pictet in December 1877. It forms a pale blue liquid, which boils at −182°·5, and has a sp. gr. at the boiling-point of 1·1181 and of 1·2386 at −210°·5; the critical temperature of the gas is −119° and the

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[1] *Journ. Soc. Chem. Ind.*, 1890, 246.
[2] *Zeit. physikal. Chem.*, 1897, **20**, 68.
[3] *Proc. Roy. Soc.*, 1893, **53**, 134.
[4] *Compt. Rend.*, 1891, **113**, 186.
[5] *Zeit. anorg. Chem.*, 1896, **12**, 1.
[6] *Compt. Rend.*, 1904, **138**, 1034.

critical pressure 58 atmospheres. When cooled by liquid hydrogen the liquid solidifies to a pale blue mass which melts below −223° and has a sp. gr. of 1·4256 at −252°·5.[1]

As long ago as 1847, Faraday discovered that oxygen is less diamagnetic than air,[2] and it was subsequently shown to be actually paramagnetic. Liquid oxygen is strongly magnetic, and, when placed in a cup-shaped piece of rock-salt between the poles of a powerful electro-magnet, suddenly leaps up to the poles and remains there permanently attached until it evaporates.[3]

Liquid oxygen presents the same absorption spectrum as the gas, characteristic bands being present in the orange, yellow, green, and blue, but the bands are much more intense and well marked than those of the gas. It also possesses a measurable thermal absorption and presents a very high resistance to an electric current. When cooled to −210° by its own rapid evaporation, it is no longer capable of supporting combustion or of combining with substances like phosphorus and sodium. Pictet[4] has indeed found that in many cases chemical action entirely ceases at temperatures approaching −150°. Thus sulphuric acid and caustic potash when compressed together at this temperature do not react, although the normal action takes place at −90°. In the same manner sodium preserves its metallic lustre in liquid alcohol of 84 per cent. at −78°, and does not commence to act upon it until the temperature reaches −48°; and alcoholic litmus solution remains blue in contact with solid sulphuric acid at all temperatures below −105°, at which reddening suddenly takes place. On the other hand, fluorine still combines violently with hydrogen below −252°·5 (p. 163).

Oxygen dissolves appreciably in water; at 0° one volume of water absorbs 0·04890 volume of oxygen, measured under the normal temperature and pressure. When the temperature rises, the quantity of oxygen absorbed becomes less, according to a complicated law, which is expressed by the empirical formula:[5]

$$C = 0{\cdot}04890 - 0{\cdot}0013413t + 0{\cdot}0000283t^2 - 0{\cdot}00000029534t^3.$$

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[1] Dewar, *Proc. Roy. Soc.*, 1904, **73**, 251.
[2] Faraday, *Phil. Mag.*, 1847 [3], **31**, 401.
[3] Dewar, *Proc. Roy. Soc.*, 1892, **50**, 247.
[4] *Compt. Rend.*, 1892, **115**, 814.
[5] L. W Winkler, *Ber.*, 1889, **22**, 1764; 1891, **24**, 3607.

Certain metals also absorb oxygen when in the molten state, and give it off again on solidifying; thus, melted silver absorbs about ten times its bulk of oxygen, and this is nearly all emitted when the metal cools, giving rise to the peculiar phenomenon of the "spitting" of silver.

As oxygen is the constituent of the air which supports combustion, it naturally follows that bodies burn in oxygen with much greater brilliancy than they do in common air. A glowing chip of wood or the red-hot wick of a taper ignites with a slight detonation when plunged into oxygen gas, and even metals such as iron, which oxidise only slowly in the air, burn brilliantly in oxygen. The following experiments serve to illustrate this property of oxygen :—

A bundle of thin iron wire, with the ends tipped with lighted sulphur or a burning piece of twine, burns when plunged into a jar of oxygen, forming the black oxide, Fe_3O_4, which falls down in glowing drops. A piece of watch-spring also burns easily with splendid scintillations if held in a flame obtained by blowing a jet of oxygen into the flame of a spirit lamp. An even more striking mode of showing the combustion of iron is to place a heap of cast-iron nails on a brick and burn them by means of a blow-pipe fed with oxygen and coal-gas contained in separate gas-holders. Substances like sulphur and phosphorus, which take fire readily in the air, burn with much greater brilliancy in oxygen; combination takes place much more rapidly, and, therefore, the temperature reached is much higher in oxygen than in the air, in which, moreover, the inert nitrogen takes up a share of the heat. The best method of exhibiting combustion in oxygen is to place the substance to be burnt in a metal cup, riveted on to an upright stem carrying a round saucer containing water. As soon as the body has been ignited, a large glass globe filled with oxygen gas is placed over it, so that the cup occupies a central position in the lower half of the globe, and then the combustion can proceed with great rapidity without fear of the globe being cracked by the heat evolved (Fig. 62). In this way sulphur burns with a bright violet flame, with formation of colourless sulphur dioxide gas, SO_2; whilst phosphorus, thus burnt, emits a brilliant white light, which vies with sunlight in intensity. In this case the white solid phosphorus pentoxide, P_2O_5, is the product of the combustion.

137 An act of chemical union accompanied by the evolution of light and heat is termed a *combustion*, and hence oxygen is

commonly termed a supporter of combustion, whilst those bodies which thus unite with oxygen are called combustible substances. A little consideration, however, shows that these terms are only relative, and an experiment makes this plain. One of the stoppered bell-jars (Figs. 63 and 64) is filled with oxygen gas, the other with hydrogen; two gas-holders, one containing hydrogen, the other oxygen, are provided with flexible gas delivery-tubes at the end of which is fixed a perforated caoutchouc stopper carrying a metal tube with a nozzle. The hydrogen gas is allowed to escape through the nozzle, then ignited, and the flame of hydrogen plunged into the bell-jar filled with oxygen, the caoutchouc stopper fitting tightly into the tubulus. A flame of hydrogen burning in oxygen is then seen, the hydrogen being the burning body and the oxygen the supporter of combustion. A stream of oxygen gas is next allowed to issue from the nozzle of the second gas-holder, the stopper of the bell-jar containing hydrogen is then removed, and the jet of oxygen is plunged into the bell-jar, whilst the flame of a candle is brought at the same instant to the tubulus. On pressing the caoutchouc stopper into its place, a flame, not to be distinguished from that burning in the other bell-jar, is seen, in which oxygen is the burning body and hydrogen is the supporter of combustion.

FIG. 62.

Most bodies do not combine with oxygen rapidly enough at the ordinary atmospheric temperature to give rise to the phenomena of combustion, but require to be heated before this begins. Oxidation is, however, often slowly going on, as in the case of the rusting of metals, the decay of wood and organic bodies. Thus, we come to distinguish between *quick* and *slow* oxidations in which the intensity of the heat and light evolved is very different.

This slow oxidation frequently occurs with gases in presence of certain finely-divided metallic particles, probably owing to the condensation of the gases on the surface or in the pores of the metal. Thus a small quantity of spongy platinum (obtained by heating the double chloride of platinum and ammonium), when held over a jet of coal-gas or hydrogen, first becomes red-hot, owing to the combustion of the gas occurring on its surface, and afterwards the temperature of the metal may rise so high that the jet of gas is ignited.

FIG. 63.

The effect of mechanical division on the combustibility of substances, especially of metals, is well known, and advantage is taken of this in the preparation of the various *pyrophori*. If tartrate of lead be gently heated in a glass tube, the lead is left in a state of very fine mechanical division, and mixed with carbon. After heating, the tube is hermetically sealed, and on cooling it may be opened and the contents shaken out into the air, when the finely divided particles will at once take fire. In the same way, if the oxides of iron, cobalt, or nickel be reduced by hydrogen at a moderate temperature, the metal is formed in a pulverulent state, in which it takes fire spontaneously on exposure to the air. The explanation of this is, that, by fine division, the ratio of the surface exposed to the mass to be heated becomes so great that the heat generated by the oxidation of the surface is sufficient to bring the mass to incandescence.

FIG. 64.

The spontaneous ignition of a mass of inflammable materials like cotton or woollen rags, when mixed with a substance, such as oil, capable of rapidly absorbing oxygen, and thereby generating heat, is one of the most common sources of fire, both in manufactories and on board ship. Similar cases of spontaneous combustion occur in hay-ricks in which the hay has been put up damp, for moisture greatly assists the process of slow oxidation. Other examples of the same thing are seen in the fires which break out in ships carrying coal, or in heaps of coal or shale; these seem to be due to the oxidation of the bituminous constituents of the coal into carbon dioxide and water by the oxygen of the air, which is absorbed by the coal, especially when much broken up, and thus evolves heat enough to set the mass on fire. All the supposed cases of spontaneous combustion occurring in the human body have been clearly proved to be mistakes or deceptions, as may be seen by reading chapter xxv. of Liebig's admirable *Letters on Chemistry*, in which this matter is fully discussed.

138 *Slow Oxidation and Autoxidation.*—In some cases the products of the slow oxidation of the substance are different from those formed by its rapid oxidation or combustion. When a coil of fine platinum wire is first heated in a flame and then hung whilst warm over the surface of some alcohol contained in a small beaker-glass, the coil soon begins to glow, and remains red-hot until all the alcohol is consumed, but no flame is seen. Alcohol has the formula C_2H_6O, and when it burns with a flame its constituents unite with oxygen to form water, H_2O, and carbon dioxide, CO_2. When oxidised at the lower temperature, a peculiar-smelling body termed aldehyde is formed, having the formula C_2H_4O; hence the oxidation of the alcohol is partial or incomplete. Only two of the hydrogen atoms of alcohol are then withdrawn, water being formed, whilst the volatile aldehyde escapes, giving rise to a peculiar choking smell.

In many cases, especially among organic compounds, it is found that if a substance capable of undergoing oxidation at the ordinary temperature is mixed with another compound which by itself is not acted on by oxygen, both substances simultaneously undergo oxidation, the absorbed oxygen being equally divided between the two components. This phenomenon is known as *autoxidation*, and the oxygen is said to be "rendered active" by the action of the first substance.

The earliest observation of this character was made by Schönbein,[1] who showed that by the oxidation of lead in presence of sulphuric acid almost the same quantity of oxygen is rendered active as is absorbed in the formation of lead sulphate $PbSO_4$. This was confirmed by Traube,[2] who proved that, in the oxidation of zinc in presence of water, zinc hydroxide and hydrogen dioxide are first formed in equal

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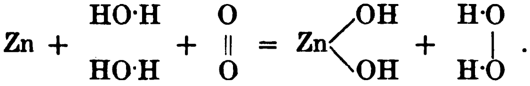
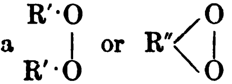
[1] *J. pr. Chem.*, 1864, **93**, 24.

[2] *Ber.*, 1893, **26**, 1471.

molecular proportions; he regarded this result as due to the occurrence of the two dependent reactions represented by the equation :



$$Zn + \begin{matrix} HO{\cdot}H \\ HO{\cdot}H \end{matrix} + \begin{matrix} O \\ \| \\ O \end{matrix} = Zn\begin{matrix} OH \\ OH \end{matrix} + \begin{matrix} H{\cdot}O \\ | \\ H{\cdot}O \end{matrix} .$$

Van't Hoff[1] concluded that in such cases the oxygen molecule is first split up into positively and negatively charged atoms (ions), and that the former unite with one constituent, and the latter with the other. Engler,[2] on the other hand, is of opinion that one of the substances (*e.g.*, the zinc in the above reaction) first combines with a molecule of oxygen, forming a peroxide of the general formula  $\begin{matrix} R'{\cdot}O \\ | \\ R'{\cdot}O \end{matrix}$ or $R''\begin{matrix} O \\ | \\ O \end{matrix}$, which readily loses one-half of its oxygen to any readily oxidisable body present, or in presence of water may yield with the latter hydrogen dioxide. That one of the two substances which combines with the oxygen molecule directly is termed by Engler the *autoxidator*, and that which undergoes oxidation by the peroxide formed, the *acceptor*. The investigation of this subject, which has been chiefly carried out with organic substances, is still in progress, and the results so far obtained are insufficient to afford a fully satisfactory explanation of all the phenomena.[3]

139 *Temperature of Ignition.*—In order that a body may take fire in air or in oxygen, a certain temperature must be reached: this point is termed the temperature of ignition. The temperature at which inflammation occurs varies widely with different substances; thus while the vapour of carbon bisulphide is ignited by bringing in contact with it a glass rod heated only to 149°, a jet of coal-gas cannot be lighted with a piece of iron at a dull red-heat: and, again, certain substances, such as the liquid phosphuretted hydrogen, or zinc ethyl, simply require to be exposed to the air at the ordinary temperature in order to ignite, whilst nitrogen can only be made to unite with oxygen by heating the mixture to the temperature of the electric

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[1] *Zeit. physikal. Chem.*, 1895, **16**, 411.

[2] Engler, *Ber.*, 1897, **30**, 1669.

[3] See Engler, *Ber.*, 1898, **31**, 3055; 1900, **33**, 1090; 1901, **34**, 2933; 1903, **36**, 2602; 1904, **37**, 49. Jorissen, *Ber.*, 1896, **29**, 1707; 1897, **30**, 1051; *Zeit. physikal. Chem.*, 1898, **22**, 56; 1899, **23**, 667. Manchot, *Annalen*, 1901, **314**, 177. Bach, *Compt. Rend.*, 1897, **124**, 2. Bodländer, *Chem. and Chem. techn. Vorträge*, **3**, 470.

arc. The temperature at which slow oxidation commences is of course lower than that of ignition ; thus phosphorus begins to enter into slow combustion in the air (exhibiting phosphorescence) below 10° C.; but we must heat it up to 60° C. before it begins to burn brightly or to enter into quick combustion.

The Davy Lamp.—A most striking example of the fact that a certain temperature must be reached before a mixture of inflammable gas with air can take fire, is seen in the safety lamp for coal mines, invented by Sir Humphry Davy.[1] The principle upon which this depends is well illustrated by holding a piece of wire gauze, containing about 700 meshes to the square inch, over a jet of gas (Fig. 65). If the gas is lit, it is possible to remove the gauze several inches above the jet, and yet the inflammable gas below does not take fire, the flame burning only above the gauze. The metallic wires in this case conduct away the heat so quickly that the temperature of the gas at the lower side of the gauze cannot rise to the point of ignition. In a similar way we may cool down a flame so much that it goes out, by placing over it a small coil of cold copper wire, whereas it is impossible to extinguish the flame if the coil of wire be previously heated. The "Davy lamp" consists of an oil lamp (Figs. 66 and 67), the top of which is inclosed in a covering of wire gauze, so that the products of combustion of the oil can escape, while no flame can pass to the outside of the gauze. Hence no ignition is possible, even if the lamp is placed in the most inflammable mixture of fire-damp and air, although the combustible gases may take fire and burn inside the gauze. It is, however, necessary to be careful that the flame thus kindled inside the gauze does not heat it up to the point of

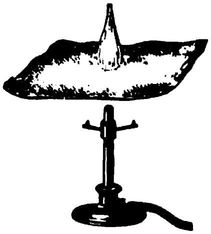

Fig. 65.

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[1] *Phil. Trans.*, 1817, pp. 45—77.

ignition of the inflammable gas, and especially to avoid placing the lamp in draughts, which might blow the flame against a point of the gauze, and thus heat it above the point of safety. Indeed, it was pointed out by Davy himself that the lamp is no longer safe if exposed to a draught of air, and several serious accidents have occurred from the neglect of these precautions. It has also been shown that the flame burning inside a wire gauze may be mechanically blown through the gauze by a current or blast of air passing at the rate of eight feet per second,[1] and this has doubtless given rise to many serious accidents. Several modifications of the original Davy lamp have been introduced to lessen this danger, but the firing of shots in fiery pits is, in any case, much to be condemned. It is almost unnecessary to say that the lamp ought not to be opened whilst in use in the pit.

FIG. 66.

FIG. 67.

140 *Heat of Combination.*—In every chemical reaction the formation of new compounds is accompanied by a change in the energy of the system. Thus when two grams of hydrogen at 0° unite with 15·88 grams of oxygen, also at 0°, to form 17·88 grams of water at the same temperature, we not only have the material conversion of the 33·3 litres of mixed gases into 17·88 c.c. of liquid water, but we find that sufficient heat is evolved to raise the temperature of 67,940 grams of water (at 0° C.) one degree. The amount of heat necessary to raise the temperature of one gram of water (at 0° C.) through one degree is called

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[1] Galloway, *Proc. Roy. Soc.*, 1874, **22**, 441.

a *calorie*, and the heat evolved in chemical reactions is measured in terms of this unit.

In order to measure the heat-change which accompanies the chemical transformation of a mixture of hydrogen and oxygen into water, oxygen is burnt in hydrogen contained in a platinum globe immersed in water contained in a calorimeter.[1] The latter consists of a gilded brass cylindrical vessel, surrounded by two concentric brass cylinders to prevent loss or gain of heat by radiation. The air in the platinum vessel is displaced by a current of hydrogen, and dry oxygen then introduced by means of a tube and ignited by an electric spark, so that the jet of oxygen continues to burn in the atmosphere of hydrogen which is supplied through another tube. The excess of hydrogen passes out of the globe by a third tube through a weighed calcium chloride tube, which retains the water vapour. The water of the calorimeter is stirred throughout the experiment.

The temperature of the water is observed just before the commencement of the combustion, and a series of observations is taken at the close of the experiment, the final temperature of the water being calculated from these after allowing for loss of heat by cooling. The amount of water formed is found by displacing the hydrogen by air and weighing the platinum globe after the experiment, the moisture carried off by the escaping gases being retained by calcium chloride and weighed. An actual experiment gave the following results:—

Initial temperature 16°·075.
Final temperature (corr.) 19°·357.
Rise of temperature 3°·282.
Water value of calorimeter 2,460 grams.
Total weight of water formed 2·129 grams.

The water value of the calorimeter represents the amount of water contained in it, together with the amount which would require as much heat to raise its temperature one degree as does the metal work of the calorimeter.

The heat developed, therefore, amounts to 2,460 × 3·282 = 8,074 cal. To this must, however, be added the heat required to raise the water produced by the combination to this final temperature, and the latent heat which was absorbed by the

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[1] Thomsen, *Thermochemische Untersuchungen*, **2**, 45.

water passing off with the hydrogen as vapour, amounting in all to 15 cal. The total heat for 2·129 grams of water is therefore 8,089 units, and hence the heat of formation of water is

$$\frac{8·089 \times 17·88}{2·129} = 67,934 \text{ cal.}$$

The mean of a number of experiments gives 67,940 cal. for the production of 17·88 grams of water. This may be expressed in an equation in the following manner, the chemical formulæ being understood to represent simply the quantities of the reacting substances and not the molecular weights :—

$$2H + O = H_2O + 67,940.$$

The product of this reaction possesses less energy than its constituents, and the mixed gases are, therefore, said to possess potential energy, which is converted on their combination into the kinetic energy or energy of motion of the molecules of the heated products. In order to reconvert the liquid water into the same weight of the mixed gases this exact amount of energy must be restored to it, and, generally, *the heat produced (or absorbed) in the formation of a compound is exactly equal to that absorbed (or evolved) by the decomposition of the substance into its original constituents.* Most substances are formed with evolution of heat, but in some cases heat is absorbed in the formation of the compound, so that it possesses more energy than its constituents. This is the case, for example, with carbon bisulphide, the oxides of chlorine and nitrogen, ozone and many other bodies. Such substances give out heat on decomposition, and consequently can often be made to undergo explosive decomposition. In these cases the heat evolved by the resolution of a small portion of the substance into its constituents is sufficient to bring surrounding parts to the decomposition point, and thus the whole mass rapidly breaks up. Chlorine monoxide, for example, gives out 17,670 cal. on decomposition:

$$Cl_2O = 2\ Cl + O + 17,670 \text{ cal.},$$

and is an exceedingly unstable compound, exploding violently when heated or even shaken.

141 It is frequently impossible to ascertain the heat of formation of a compound directly, but an indirect determination is

rendered possible by the fact that *the heat evolved in a chemical reaction depends only on the initial and final states of the system, and is independent of the intermediate stages.*[1] (Law of Hess.)

Thus if we wish to find the heat evolved in the production of a dilute solution of ammonium chloride from the two gases, ammonia and hydrogen chloride, we may either (1) allow these two gases to combine directly and dissolve the product in water, or (2) dissolve the two gases separately in water and mix the solutions. In both cases we start with ammonia, hydrochloric acid gas, and water, and end with a dilute solution of ammonium chloride, and the amount of the heat-change is found to be the same in both cases.

The determination of the heat of formation of hydriodic acid gas from its elements may serve as an instance of the application of this indirect method.

When hydriodic acid, dissolved in water, is decomposed by chlorine we have the reaction:—

$$\mathrm{HI, Aq} + \mathrm{Cl} = \mathrm{HCl, Aq} + \mathrm{I} + 26{,}000 \text{ cal.}$$

In this reaction the hydriodic acid has been decomposed and the hydrogen and chlorine have combined to form hydrochloric acid which has dissolved in the water. The second part of this change gives rise to 39,000 cal.

$$\mathrm{H} + \mathrm{Cl} + \mathrm{Aq} = \mathrm{HCl, Aq} + 39{,}000 \text{ cal.}$$

From this it follows that the heat absorbed in the decomposition of the aqueous hydriodic acid into hydrogen and iodine is $39{,}000 - 26{,}000 = 13{,}000$ cal., and therefore that the heat of formation of the dilute acid is accompanied by an evolution of 13,000 cal.

$$\mathrm{H} + \mathrm{I} + \mathrm{Aq} = \mathrm{HI, Aq} + 13{,}000 \text{ cal.}$$

It has further been found that the solution of hydriodic acid gas in water gives rise to an evolution of 19,060 cal., so that the actual formation of the gas from its elements is accompanied by a heat-change of $13{,}000 - 19{,}060 = -6{,}060$ cal. Gaseous hydriodic acid is, therefore, produced from solid iodine and gaseous hydrogen with absorption of this amount of heat.

This branch of chemical science, which is known as *Thermo-*

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[1] Hess, *Pogg. Ann.*, 1840, **50**, 385.

chemistry, has been studied by many chemists, among whom may be mentioned Andrews, Favre and Silbermann, Julius Thomsen, and Berthelot, from whose researches the numbers given in the following table are taken.[1]

Molecular Heat of Formation from the Elements.

HCl	21835	PCl_5	104213
HBr	8337	$POCl_3$	144905
HI	− 6060	As_4O_6	308626
O_3	− 29378	As_2O_5	217755
H_2O	67940	AsH_3	− 43770
H_2O_2	− 22927	B_2O_3	314821
Cl_2O	− 17670	CH_4	21637
I_2O_5	44961	C_2H_4	− 2679
SO_2	70567	CO_2	
SO_3	102526	(*a*) charcoal	96253
NH_3	11910	(*b*) gas carbon	95806
N_2O	− 17965	(*c*) diamond	93190
NO	− 21438	(*d*) graphite	92660
NO_2	− 2035	CO	67490
N_2O_5	13000	CS_2	− 2581
PH_3	4267	$COCl_2$	55183
P_2O_5	177062	CCl_4	20843
PCl_3	74933		

THE OXIDES.

142 All the elements with the exception of fluorine and the members of the helium group are found to unite with oxygen to form an important class of compounds termed *oxides*, possessing very various properties according to the nature of the combining element and the quantity of oxygen with which it unites. In many instances one element is found to combine with oxygen in several proportions, giving rise to distinct oxides. Oxides may be divided into three classes, distinguished as *Basic oxides*, *Peroxides*, and *Acid-forming oxides.*

(1.) *The basic oxides*, such as K_2O, potassium oxide; BaO,

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[1] These numbers have been recalculated from the original results on the basis of O = 15·88.

barium oxide; Fe_2O_3, ferric oxide, form in combination with water a class of compounds termed ***hydroxides*** or ***hydrated oxides***, such as caustic potash, KOH; barium hydroxide or caustic baryta, $Ba(OH)_2$; ferric hydroxide, $Fe(OH)_3$; thus:

$$K_2O + H_2O = 2KOH.$$
$$BaO + H_2O = Ba(OH)_2.$$
$$Fe_2O_3 + 3H_2O = 2Fe(OH)_3.$$

The characteristic property of these oxides as well as of the corresponding hydroxides is their power of neutralising acids and forming compounds which are termed salts.

(2.) *The peroxides* contain more oxygen than the basic oxides. A portion of it is loosely combined and is given off on heating; thus $3MnO_2 = Mn_3O_4 + O_2$; and although they can form hydroxides, these peroxides have not generally the power of neutralising acids and forming stable salts. The following is a list of some of the more important *peroxides*:—Barium dioxide BaO_2; potassium tetroxide K_2O_4; sodium peroxide Na_2O_2; manganese dioxide MnO_2; lead dioxide PbO_2. The term peroxide is a somewhat vague one, and is applied to oxides possessing very different properties.

(3.) *The acid-forming oxides* combine with water to form hydrates, which are termed *acids;* thus—

Sulphur trioxide SO_3 yields Sulphuric acid H_2SO_4.
Nitrogen pentoxide N_2O_5 yields Nitric acid HNO_3.
Phosphorus pentoxide P_2O_5 yields Phosphoric acid H_3PO_4.

$$SO_3 + H_2O = H_2SO_4.$$
$$N_2O_5 + H_2O = 2HNO_3.$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

Acids possess a sour taste, turn blue litmus red, and neutralise the basic oxides, which when they are soluble have the opposite property and turn red litmus blue. They all contain hydrogen which can be replaced by metals.

Salts may be considered to be acids in which the hydrogen is replaced by a metal. The most important methods by which they can be obtained have already been considered (p. 205).

The division into these three classes of oxides cannot, however, be strictly carried out. Thus, whilst the position of the extreme members of each series, such as the strong bases or alkalis on the one hand, and the acids on the other, can be sharply defined, it is often difficult to classify the middle terms such as alumina, Al_2O_3, manganese dioxide, MnO_2, and tin oxide, SnO_2, which act sometimes as weak bases and at other times as weak acids.

OZONE. $O_3 = 47{\cdot}64$ (H = 1).

143 So long ago as 1785, Van Marum observed that oxygen gas through which an electric spark had been passed possessed a peculiar smell, and at once tarnished a bright surface of mercury; but it was not until the year 1840 that the attention of chemists was recalled to this fact by Schönbein.[1] This chemist showed that the peculiar strongly-smelling substance, to which he gave the name of ozone (from ὄζω, I smell), is capable of liberating iodine from potassium iodide, and of effecting many other oxidising actions. Schönbein and other workers have shown that ozone is also produced in many other ways.

(1) It is evolved at the positive pole in the electrolysis of acidulated water.

(2) It is formed by the discharge from an electrical machine through air or through oxygen gas.

(3) When fluorine is passed into water at 0°, the oxygen liberated contains 10 to 14 per cent. of ozone.[2]

(4) By acting with strong sulphuric acid upon dry barium dioxide, oxygen is given off which contains a considerable quantity of ozone.

(5) When oxygen is passed over heated manganese dioxide, cobalt oxide or certain other metallic oxides some ozone is produced.[3]

(6) Ozone is obtained when potassium permanganate and sulphuric acid are distilled together in a vacuum.[4]

(7) It is also stated that ozone is formed during combustion, and can be recognised by its smell when a current of air is blown through the upper portion of a flame.

144 Powerful oxidising agents are produced on the oxidation of phosphorus, turpentine and other oils by atmospheric oxygen, and these were formerly thought to be ozone.

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[1] *Pogg. Ann.*, 1840, **50**, 616.

[2] Moissan, *Compt. Rend.*, 1899, **129**, 570.

[3] Brunck, *Zeit. anorg. Chem.*, 1895, **10**, 222.

[4] Frye, *Chem. News*, 1896, **73**, 122.

In the case of phosphorus, Van t'Hoff[1] has found that the amount of oxygen rendered active is equal to one atom for every two atoms of phosphorus oxidised, and is independent of the nature of the acid produced. From these experiments, and from those of Ewan[2] on the rate of oxidation of phosphorus, he considers the activity to be due to free oxygen atoms, or oxygen ions and not to ozone. With turpentine and similar essential oils,[3] on the other hand, the activity appears to be due to the combination of the oxygen with the oil to form a substance of the nature of a peroxide.

145 For many years much doubt existed respecting the exact chemical nature of this oxidising principle. Williamson and Baumert came independently to the conclusion that ozone is an oxide of hydrogen having the formula H_2O_3; while Marignac and De la Rive, as well as Frémy and Becquerel, and more recently Shenstone[4] and Baker,[5] found that ozone is formed when electric sparks are passed through perfectly dry oxygen gas. The explanation of these contradictory results lies in the fact that it was found impossible to obtain ozone except in very small quantities, and that an exact investigation of its composition is rendered still more difficult by its extremely energetic properties. Further researches, conducted with the greatest care, have, however, shown that ozone is nothing more than condensed oxygen, and the steps by which this conclusion has been arrived at constitute an admirable example of the successful resolution, by the convergence of many independent investigations, of an apparently insoluble problem.

To Andrews[6] belongs the credit of having first proved that ozone, from whatever source derived, is one and the same body, having identical properties, and the same constitution, and also that it is not a compound of two or more elements, but oxygen in an altered and allotropic condition.

If a series of electric discharges be sent through a tube containing pure and dry oxygen, only a small portion of the gas is converted into ozone; but if the ozone is removed as soon as it is formed, by a solution of iodide of potassium, for example, the

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[1] *Zeit. physikal. Chem.* 1895, **16**, 411.

[2] Ewan, *Zeit. physikal. Chem.* 1895, **16**, 315.

[3] Engler and Weissberg, *Ber.* 1898, **31**, 3046.

[4] *Journ. Chem. Soc.* 1893, 938.

[5] *Journ. Chem. Soc.* 1894, 617.

[6] *Phil. Trans.* 1856, 13.

whole of the oxygen can be gradually converted into ozone. In order to obtain the maximum production of ozone, pure oxygen gas is allowed to pass through an apparatus (Fig. 68), which consists essentially of an iron tube (BB) turned very truly on the outside, through which a current of cold water can be passed by means of the tubes (CC). Outside this metal cylinder is one of glass (AA) very slightly larger than the iron one. By means of tubes (DD) air or oxygen can be passed through the annular space between the two cylinders. Part of the outer cylinder at G is covered with tinfoil. The outer tinfoil coating and the inner metal cylinder are connected with the poles of an induction coil at E and F. By this means the oxygen is subjected to a series of silent discharges, by which it is converted partially into ozone.

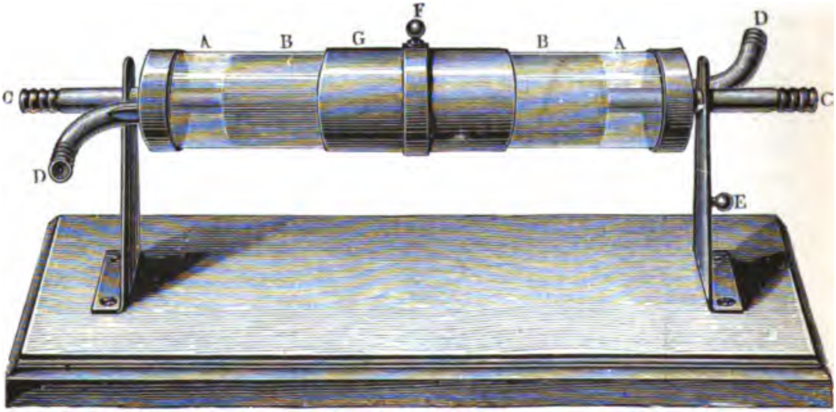

FIG. 68.

The action of this stream of ozonised oxygen upon a sheet of paper covered with a solution of iodide of potassium and starch is strikingly shown when the paper is held in front of the current of issuing gas, the white surface instantly assuming a deep blue colour.

Modifications of the above apparatus for obtaining ozonised oxygen on the large scale have been devised by numerous workers.

The best yield of ozone is obtained[1] by using tubes of very thin glass and fitting closely into each other so that the path of discharge is short, employing at the same time a high difference of potential, and maintaining the temperature at 0°; dilution

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[1] Shenstone and Priest, *Journ. Chem. Soc.* 1893, 938.

of the oxygen with nitrogen favours the production of ozone,[1] and, although ozone is formed from carefully dried oxygen, the yield is much greater if the gas is used in a moist state. Under the above conditions, using moist air, 98 per cent. of the oxygen may be converted into ozone.

According to Goldstein,[2] oxygen may be completely converted into ozone by passing it into an evacuated Geissler tube, partially immersing it in liquid air until the pressure is reduced to a few centimetres, and then passing an electrical discharge through the tube. The pressure immediately falls, and at this temperature the ozone separates as a dark blue liquid. Fresh oxygen may then be added and the process repeated until a sufficient quantity of liquid ozone is formed.

146 That this ozonisation is accompanied by a change of bulk was shown by Andrews and Tait.[3] These chemists filled a glass tube (Fig. 69) with dry oxygen; one end was then sealed off, whilst the other ended in a capillary tube, bent in form of a syphon, and containing a liquid, such as strong sulphuric acid, upon which ozone does not act. On passing through the gas a silent discharge, obtained by attaching one platinum wire to one pole of a Ruhmkorff's coil, or to the conductor of a frictional electrical machine, a gradual diminution of volume occurred, but this never reached more than $\frac{1}{12}$ of the whole. After the ozonised gas was heated to about 300° C. it was found to have returned to its original bulk, and had lost all its active properties.

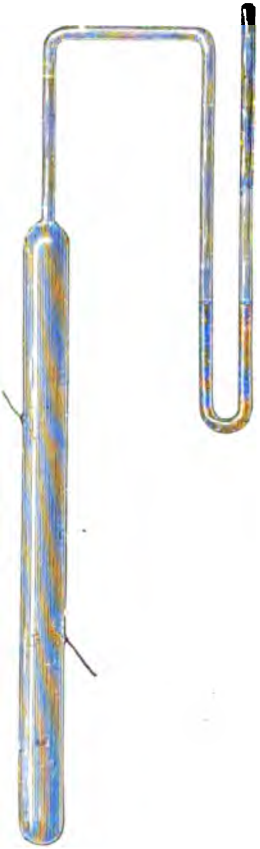

FIG. 69.

This decomposition of ozone into oxygen can be readily shown

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[1] Shenstone, *Journ. Chem. Soc.* 1897, 472; Shenstone and Evans, *Journ. Chem. Soc.* 1898, 246.

[2] *Ber.* 1903, 36, 3042.

[3] *Phil. Trans.* 1860, 113.

by allowing a stream of ozonised oxygen to pass through a tube heated by the flame of a Bunsen-lamp. Every trace of heightened oxidising action will disappear and the blue iodide of starch will not be formed; whilst on removing the hot tube an immediate liberation of iodine will be observed, if the prepared paper is again brought into contact with the issuing gas. In order to gain a knowledge of the composition of ozone, Andrews introduced into his ozone tube a sealed glass bulb containing substances able to destroy the ozone, such as iodide of potassium solution, or metallic mercury. After transforming into ozone as much as possible of the oxygen contained in this tube, the bulb filled with the iodide of potassium solution was broken and the iodine liberated by the ozone. On observing the column of sulphuric acid in the syphon tube it was found to have remained unaltered after the ozone had reacted, showing that the change had not been attended with any alteration in volume, whilst on afterwards heating up to 300° C. and then allowing to cool, no further increase in the volume occurred, proving that all the ozone had been decomposed.

These facts are explained by the supposition that, in the formation of ozone, three volumes of oxygen condense to form two volumes of ozone,

$$\underset{\text{3 vols.}}{3O_2} = \underset{\text{2 vols.}}{2O_3}$$

which, when heated, increase in bulk again to form the original three volumes of oxygen, whilst, when acted upon by neutral potassium iodide, one-third of the ozone is spent in liberating the iodine, and the other two-thirds go to form ordinary oxygen, thus:—

$$O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH.$$

This supposition has been proved to be correct by Soret, as follows: many essential oils, such as turpentine and oil of thyme, had been observed by Schönbein to possess the property of absorbing ozone without decomposing it, and Soret[1] showed that the *diminution* in volume which takes place on the absorption of the ozone from a measured quantity of ozonised oxygen by these oils is exactly twice as great as the *increase* of volume observed when the ozone is decomposed by heating the gas. A series of three experiments proved that for every 19·3 c.c. of

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[1] *Ann. Chim. Phys.* 1866, [4], **8**, 113; *Phil. Mag.* 1866, [4], **31**, 82, and 1867, **34**, 26.

ozone absorbed by the oil, an increase of volume of 9·47 c.c., instead of the exact number 9·65 c.c., was obtained on heating. Hence, ozone possesses the molecular formula O_3, three volumes of common oxygen having been condensed to two volumes by the formation of ozone.

Soret obtained a confirmation of his results from a totally different point of view.[1] If the density of ozone is one-and-a-half times as great as that of common oxygen, the rate of diffusion (p. 90) will be inversely as the square roots of these numbers; if, therefore, we know the rate at which ozone diffuses, compared with the rate of diffusion of another gas whose density is also known, we can draw conclusions respecting the density of ozone. The gas chosen for experiment was chlorine, and it was found by experiment that 227 volumes of chlorine diffused in the same time as 271 volumes of ozone, or for one volume of ozone there diffused 0·8376 volume of chlorine; hence, according to the law of inverse squares of the densities, the density of ozone is 24·8, for

$$1 : 0{\cdot}8376 : : \sqrt{35{\cdot}18} : \sqrt{24{\cdot}8}$$

whereas from the formula O_3 it should be the half of 3 × 15·88, that is, 23·82.

Brodie [2] arrived, by a long series of most exact determinations, at the same result, inasmuch as he obtained the ratio of 1 to 2 between the volume of the oxygen used in liberating iodine from potassium iodide and that of the ozone absorbed by turpentine, and also showed that all the oxidising effects of ozone upon the most various substances can be explained upon this basis.

These experiments prove conclusively that dry oxygen is converted by the action of the silent electric discharge into an allotropic modification. But they do not decide the question whether the strongly-smelling body obtained in the electrolysis of water has an analogous constitution, or whether it may not be an oxide of hydrogen. Andrews, however, proved that if such electrolytic oxygen is perfectly dried it does not lose its powerful smell, and that if the dried gas be then passed through a hot glass tube, the smell, as well as the oxidising power, altogether disappears without the smallest trace of moisture being formed, and this must have been deposited if the electrolytic oxygen had contained an oxide of hydrogen.

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[1] *Ann. Chim. Phys.* 1868, [4], **13**, 257.

[2] *Phil. Trans.* 1872, Part ii. 435.

147 *Properties.*—Ozone prepared by any of the above methods is a gas possessing a peculiar odour, somewhat resembling that of very diluted chlorine. It has a faint blue colour, which is rendered more evident by compression. Ozone, on keeping, changes gradually into ordinary oxygen, but the presence of water retards this transformation in a marked manner.[1]

Not only is ozone destroyed by heat, but also when agitated strongly with glass in fine fragments (Andrews). It is one of the most powerful oxidising agents known; it attacks and at once destroys organic substances such as caoutchouc, paper, &c. One of the most characteristic actions of ozone is its effect on mercury. The metal at once loses its mobility and adheres to the surface of the glass in a thin mirror, and so delicate is this reaction, that a single bubble of oxygen containing $\frac{1}{30}$th of its bulk of ozone will alter the physical characters of several pounds of mercury, taking away its lustre and the convexity of its surface; on shaking the mercury with water it regains its original condition.[2]

In many of its oxidising actions the volume of ozone does not undergo any alteration, one molecule of ozone, O_3, yielding one molecule of ordinary oxygen, O_2, and one atom of oxygen being employed for the oxidation. Ozone is converted into ordinary oxygen by contact with certain metallic oxides, such as oxide of silver and manganese dioxide or with platinum black. These substances are not permanently altered by the reaction, which is probably of somewhat the same nature as that by which potassium chlorate is decomposed at low temperatures in the presence of certain bodies (p. 237). Some nonmetals as well as most metals are at once oxidised in presence of moist ozone: silver to silver oxide,[3] phosphorus to phosphoric acid, sulphur to sulphuric acid,[4] sulphides to sulphates, aqueous ammonia to ammonium nitrite and nitrate,[5] and ferrocyanides to ferricyanides, whilst certain organic sulphides[6] yield sulphuric acid, and others free sulphur.

Ozone also combines in equal molecular proportions with certain organic compounds to form *ozonides*,[7] which react with

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[1] Shenstone, *Journ. Chem. Soc.* 1897, 472.

[2] Baker, *Journ. Chem. Soc.* 1894, 617.

[3] Frémy, *Compt. rend.* 1865, **61**, 939; Schöne, *Ber.* 1880, **13**, 1503.

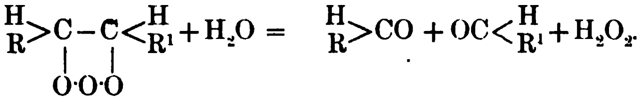
[4] Weyl, *Chem. Zeit.* 1901, **25**, 292.

[5] Ilosva, *Ber.* 1894, **27**, 3500.

[6] Weyl, *loc. cit.*

[7] Harries, *Ber.* 1904, **37**, 839.

water, forming oxidation products of the compounds together with hydrogen peroxide, thus:—



$$\begin{array}{l} {}^{H}_{R}\!>C-C<^{H}_{R^1}+H_2O = {}^{H}_{R}\!>CO+OC<^{H}_{R^1}+H_2O_2. \\ \qquad | \quad\; | \\ \quad\;\; O{\cdot}O{\cdot}O \end{array}$$

Ozone has not, however, according to the experiments of Carius,[1] the power it was formerly supposed to possess, of oxidising nitrogen to nitric acid in presence of water.

To distinguish between ozone, hydrogen peroxide and oxides of nitrogen, which have the common property of liberating iodine from potassium iodide, several tests have been proposed. Engler and Wild[2] state that on passing a mixture of ozone and hydrogen peroxide through a solution of chromic acid, the hydrogen peroxide is decomposed whilst the ozone is unaltered. The use of certain organic compounds has been proposed by Arnold and Mentzel;[3] thus, test-papers soaked in an alcoholic solution of benzidine turn brown with ozone, blue with nitrous fumes, and are unchanged by hydrogen peroxide, whilst a solution of benzidine and copper sulphate gives a blue precipitate with hydrogen peroxide, and a reddish-brown precipitate with ozone.

Ladenburg and Quasig[4] have shown that the reaction:—

$$O_3+2KI+H_2O=O_2+I_2+2KOH.$$

takes place only in neutral solution, if the solution be acid the ozone reacts with the hydriodic acid formed thus:—

$$4O_3+10HI+H_2O=5I_2+H_2O_2+5H_2O+3O_2.$$

Ozone therefore may best be estimated by passing it into a neutral solution of potassium iodide, acidifying, and estimating the free iodine by titration with sodium thiosulphate.

Ozone is somewhat soluble in water, imparting to the latter its peculiar odour as well as its oxidising powers. According to Ladenburg,[5] 1,000 volumes of water dissolve 10 volumes of ozone; Inglis[6] finds, however, that there is a slow action between water and ozone.

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[1] *Annalen*, 1875, **179**, 1.

[2] *Ber.* 1896, **29**, 1940.

[3] *Ber.* 1902, **35**, 1324, 2902.

[4] *Ber.* 1901, **34**, 1184.

[5] Ladenburg, *Ber.* 1898, **31**, 2508.

[6] *Journ. Chem. Soc.* 1903, 1010.

One of the uses to which ozone has been put is the sterilisation of water on the large scale[1]; on passing a current of ozonised oxygen through water all pathogenic organisms are destroyed, and the organic matter present considerably diminished in quantity.

Ozone forms on condensation an indigo-coloured liquid (Hautefeuille and Chappuis), which boils at −119° (Troost),[2] and like liquid oxygen is strongly magnetic.[3] The compression of the gas must be effected slowly, or the heat produced raises its temperature to such a point that the gas is suddenly converted into ordinary oxygen with explosion. On the evaporation of liquid ozonised oxygen, the oxygen boils off first, then the temperature rises to the boiling point of ozone and an explosion occurs.[4] A considerable amount of heat is evolved in this change, ozone being formed from oxygen with absorption of 29,378 cal. (Berthelot).

$$3O_2 = 2O_3 - 2 \times 29378.$$

It is found that the change of one allotropic form of a substance into another is always accompanied by either an evolution or an absorption of heat.

Richarz and Schenck[5] state that ozone exhibits properties of radioactivity.

Schönbein, and certain other chemists, believed that another modification of oxygen besides ozone existed, to which they gave the name of *ant-ozone*, the chief peculiarity of this body being its power of combining with ozone to form ordinary oxygen. Further experiments have, however, proved that ant-ozone is nothing more than hydrogen dioxide.[6]

148 *Atmospheric Ozone.*—The difficult question as to whether ozone exists in the atmosphere can scarcely be regarded as settled in the affirmative; hydrogen peroxide is probably present, whilst the higher oxides of nitrogen are certainly formed in the atmosphere by electrical discharges, and the tests hitherto used for the detection of atmospheric ozone

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[1] Marmier and Abraham, *Compt. rend.* 1899, **128**, 1034. Proskauer, *Ber. Deutsch. Pharm. Ges.* **13**, 259.

[2] Troost, *Compt. rend.* 1898, **126**, 1751.

[3] Dewar, *Proc. Roy. Soc.* 1892, **50**, 261.

[4] Ladenburg, *Ber.* 1898, **31**, 2508.

[5] *Sitz. K. Akad. Wiss. Berlin*, 1903, 1102.

[6] See Brodie, *Phil. Trans.* 1862, 837.

would be given equally well by either hydrogen peroxide or the higher oxides of nitrogen or both.

The experiments of Andrews[1] have, however, decisively proved that an oxidising substance does occur in the atmosphere which agrees in many of its properties with ozone. Thus when air at the ordinary temperature was passed over ozone test-papers contained in a glass-tube, an indication of ozone was seen in two or three minutes. When the air before passing over the test-paper was heated to 260° C. not the slightest action occurred on the test-paper, however long the current was allowed to pass. On the other hand, when air mixed with very small quantities of chlorine or the higher oxides of nitrogen was drawn over the papers, they were geneally affected whether the air had been previously heated or not. These experiments, however, would equally serve to show the presence of hydrogen peroxide, which would be destroyed by heating as well as ozone. Houzeau has shown that a neutral solution of iodide of potassium on exposure to air becomes alkaline with the liberation of iodine, an effect which would not be produced by the oxides of nitrogen, and which he believed to be due to the presence of ozone in the air, but which would be also caused by hydrogen peroxide.

In spite of the uncertainty as to whether ozone really exists in the air, many methods have been given for its determination, and many statements have been made as to the proportion of ozone present.[2]

The usual method of estimating the amount of active oxidising substances present in the air is a very rough one. It consists in exposing to the air papers which have been impregnated with a solution of starch and potassium iodide, for a given time (and best in the dark), and noting the tint which they assume compared with certain standard tints. The papers prepared according to the directions of Dr. Moffat are those on which most reliance is placed. Both hydrogen peroxide and the higher oxides of nitrogen, however, would give this test, so that it is doubtful how far the iodine is really liberated by ozone.

It is scarcely necessary to remark that in thickly-inhabited districts, especially in towns where much coal is burnt, ozone

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[1] *Proc. Roy. Soc.*, 1868, **16**, 63.

[2] Neumann, *Pogg. Ann.* 1857, **102**, 614. Poëy, *Compt. rend.* 1867, **65**, 708. Smyth, *Proc. Meteoro. Soc.* June 16th, 1869. Thierry, *Compt. rend.* 1897, **124**, 460.

must in any case almost always be absent, as it is reduced to ordinary oxygen by the organic emanations as well as by the sulphurous acid constantly present in such air.

Some observers state that in the air of the country, and especially in sea air, the presence of ozone can almost always be recognised, often indeed by its peculiar smell, this being said by them to be the most reliable test for its presence.

HYDROGEN AND OXYGEN

These elements form two compounds.

(1) HYDROGEN MONOXIDE or WATER, H_2O, and
(2) HYDROGEN DIOXIDE, H_2O_2.

WATER. $H_2O = 17{\cdot}88$.

149 The question of the discovery of the composition of water, a substance which up to nearly the end of the eighteenth century was considered to be a simple body, has been fully discussed in the historical introduction. We there learned that Cavendish first ascertained that by the combustion of two volumes of hydrogen and one volume of oxygen, pure water and nothing else is produced. Warped, however, as his mind was with the phlogistic theory, he did not fully understand these results, and the true explanation of the composition of water was first given by Lavoisier in 1783, when the French chemist repeated and confirmed the experiments of Cavendish. The apparatus, of much historical interest, used by him for proving that hydrogen gas is really contained in water, is seen in facsimile in Fig. 70. The water contained in the vessel *a* was allowed to drop slowly into the tube, *e d*, from which it flowed into the gunbarrel, *d f*, heated to redness in the furnace. Here part of the water was decomposed, the oxygen entering into combination with the metallic iron, whilst the hydrogen and some undecomposed steam passed through the worm, *s*, where the steam was condensed and the hydrogen was collected and measured in the glass bell-jar, *m*. The result of these experiments was found to be that 13·13 parts by weight of hydrogen united to 86·87

parts by weight of oxygen, or 12 volumes of oxygen with 22·9 volumes of hydrogen.[1]

Cavendish, by exploding air with hydrogen by means of the electric spark had, on the other hand, come to the conclusion that the relation by volume of the two gases combining to form water was 1 of oxygen to 2 of hydrogen, and this was confirmed in 1805 by the more exact experiments of Gay-Lussac and Humboldt.[2]

The formation of water by the combustion of hydrogen in the air can be readily observed by means of the arrangement shown in Fig. 71. The hydrogen is dried by passing through the horizontal tube filled with pieces of chloride of calcium, then ignited at the end of the tube, and the flame allowed to burn under the bell-jar. By degrees drops of water form, these collect on the sides of the glass, and drop down into the small basin placed beneath. Another apparatus for exhibiting the same fact is seen in Fig. 72. It consists of a glass gasholder filled with hydrogen, which is dried by passing through the chloride of calcium tube (*b*), and then burns under the glass funnel (*c*). The water formed collects in the tube (*e*), an aspirator (*f*) drawing the steam formed by the combustion through the tube (*d*).

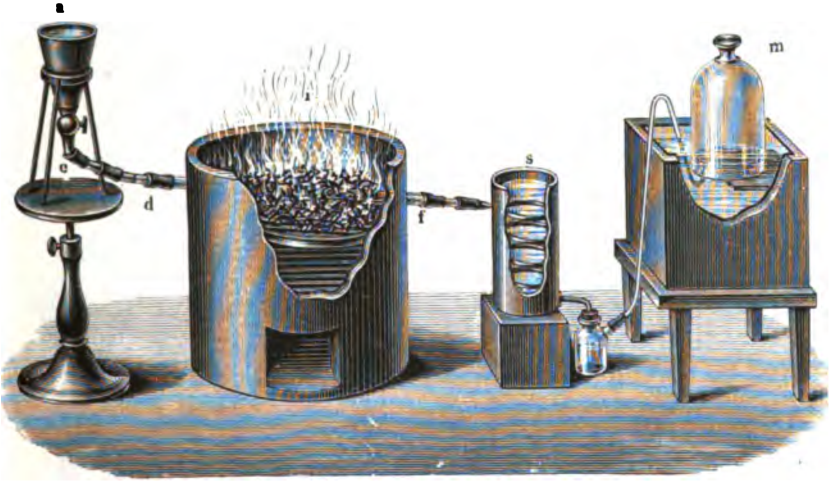

FIG. 70.

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[1] Mémoire par MM. Meusnier et Lavoisier. *Mém. de l'Acad. de Sciences*, année 1781, p. 269, lu le 21 Avril, 1784.

[2] *Journ. de Phys.* **60**, 129.

150 *Eudiometric Synthesis of Water.*—The method which Cavendish used for the purpose of ascertaining the composition of water is still employed in principle, although the modern processes are much superior in accuracy to the older ones. Bunsen's modification of the method consists in bringing known volumes of the constituent gases successively into a eudiometer, allowing these gases to combine under the influence of

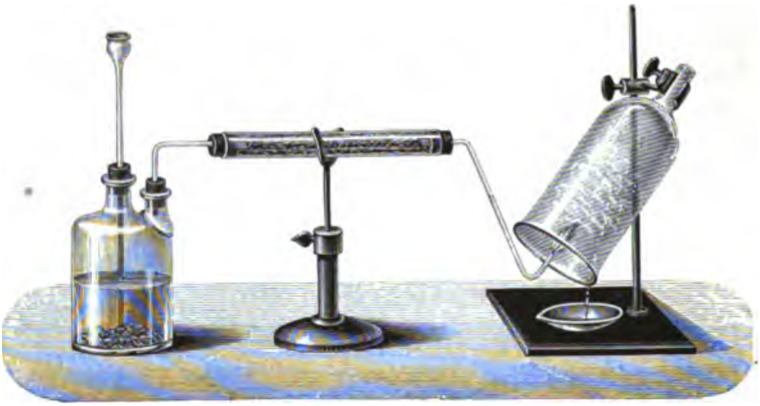

FIG. 71.

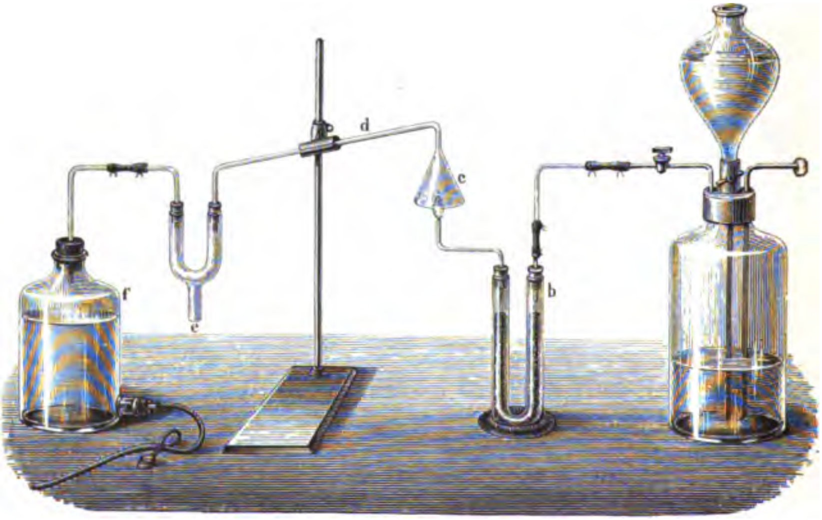

FIG. 72.

the electric spark and carefully observing the consequent change of volume. The eudiometer employed is a strong glass tube (*c*), Fig. 73, one metre in length and 0·025 m. in breadth, closed at the top and open at the bottom, having platinum wires sealed through the glass near the closed end. The tube is accurately divided into divisions of length by etching a millimetre scale on the glass, and the capacity of each division of length on the scale is ascertained by a process of calibration, consisting in pouring successively exactly the same volume of mercury into the tube, until the whole is filled with the metal, the height to which each volume of mercury reaches being carefully read off on the millimetre scale etched on the glass.

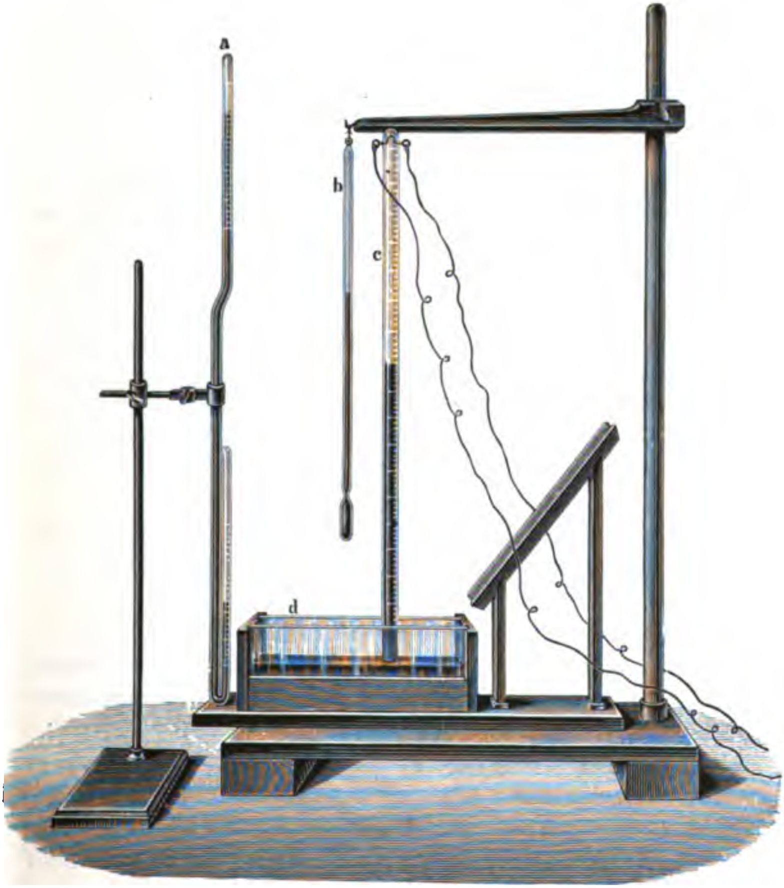

FIG. 73.

The eudiometer containing at the top one drop of water to render the gases moist, is first completely filled with mercury and inverted in the pneumatic trough (*d*) containing the same metal. Then a certain volume of perfectly pure oxygen gas, prepared from pure potassium chlorate, is introduced, the volume is read off, and the necessary reductions for temperature and pressure are made. For this purpose a thermometer (*b*) is hung up near the eudiometer, and the temperature as well as the level of the meniscus of mercury in the tube read off by means of a telescope placed in a horizontal position at such a distance that the radiation from the observer does not produce any sensible effect on the reading. The pressure to which the gas is subjected is then ascertained by reading off the height of the barometer (*a*) also placed near the eudiometer, and subtracting from this the height of the column of mercury in the eudiometer above the level of the mercury in the trough, this height being obtained by reading the millimetre divisions at the upper and lower levels of the mercury. The temperature of the mercurial columns in the barometer and eudiometer must also be observed, so that correction may be made for the expansion of the mercurial column the height of which must be reduced to that of a column at 0° C.

We have now, taking an actual example :—

(1) The observed volume of moist oxygen taken from the reading of the upper level of mercury and from the calibration-table of the eudiometer = 399·1.

(2) The temperature of the gas = 15° C.

(3) The height of the barometer (corrected to 0° C.) = 765 mm.

(4) The height of the mercury column in the eudiometer (corrected to 0° C.) = 500 mm.

From these data it is easy to obtain the volume of the gas at the normal temperature (0°) and under some standard pressure (either 1 m. or 760 mm. of mercury at 0°). The gas has, however, been measured in the moist state ; the water vapour present exerts a certain pressure, and thus depresses the column of mercury in the eudiometer and increases the apparent pressure of the gas. In order, therefore, to obtain the actual pressure of the dry gas it is necessary to subtract from the height of the barometer the column of mercury in the eudiometer and the vapour pressure of the water at the temperature of the experiment, which may be found in a table of vapour pressures (p. 301). This amounts at 15° to 12·7 mm. of mercury, so that the true pressure of the gas considered dry is:

$$765 - 500 - 12{\cdot}7 = 252{\cdot}3 \text{ mm.}$$

Applying the laws of Boyle and Dalton, it appears that 399·1 vols. of gas at 15° and 252·3 mm. pressure will, at 0° and a pressure of 1 metre of mercury, occupy a volume of:

$$\frac{399{\cdot}1 \times 273 \times 252{\cdot}3}{288 \times 1000} = 95{\cdot}45.$$

The second part of the process consists in adding a volume of pure hydrogen, care being taken not to allow any bubbles of gas to remain attached to the sides of the tube. The volume of hydrogen added must be such that the inflammable mixture of two volumes of hydrogen and one volume of oxygen shall make up not more than from 30 to 40 per cent. by volume of the whole gas, otherwise the mercury is apt to be oxidised by the high temperature of the explosion. Thus supposing we had five volumes of oxygen, we must add ten volumes of hydrogen to combine with this, and $\frac{65 \times 15}{35} = 28$ volumes for the purpose of dilution.

As soon as the temperature equilibrium has been established, the volume of the mixed gases contained in the eudiometer is again read off with the same precautions, and the temperature and pressure again ascertained as before. This having been accomplished, the open end of the eudiometer is firmly pressed down below the mercury in the trough upon a plate of caoutchouc, previously moistened with corrosive sublimate solution, and held firmly in this position by a stout clamp. By means of an induction coil an electric spark is then passed from one platinum-wire through the gas to the other wire; the mixed gases are thereby ignited, and a flame is seen to pass down the tube. On allowing the mercury from the trough again to enter freely at the bottom of the tube a considerable diminution of bulk is observed. The eudiometer is then allowed to remain untouched until the temperature of the gas has again attained that of the surrounding air, and the volume, pressure, and temperature are ascertained as before. The volume which has disappeared does not, however, exactly correspond to the true volume of the gases which have united, inasmuch as the water formed occupies a certain, although a very small, space. In order to obtain the exact volume of the combined gases, the volume of the explosive gases before the explosion must be multiplied by the number 0·0005, which represents the fraction of the total bulk of the component gases which is occupied by the liquid water formed, and this volume must then be added to the observed contraction. For other corrections the article on this subject in Bunsen's Gasometry must be consulted.

The following numbers illustrate the course of such an experiment:—

Synthesis of water by volume.

	Reduced to 0° and 1 m. of mercury.
Volume of oxygen taken	95·45
Volume of oxygen and hydrogen .	557·26
Volume after the explosion . . .	271·06

Hence 286·2 volumes disappeared, or 95·45 volumes of oxygen have combined with 190·75 of hydrogen. Consequently 1·0000 volume of oxygen combines with 1·9963 volumes of hydrogen to form water.

By careful repetition of the above experiments the composition of water by volume was ascertained, within very narrow limits, to be in the proportions of one of oxygen to two of hydrogen.

Since the knowledge of the exact composition of water by volume is of the greatest importance for the determination of the atomic weight of oxygen, many attempts have been made to devise more accurate methods than that above described for ascertaining the exact ratio in which hydrogen and oxygen combine by volume.

The most accurate of these is due to Scott,[1] who has retained the principle of the eudiometric method, but greatly improved its details. The oxygen was prepared by heating silver oxide, and the hydrogen by the action of steam on sodium, and was sometimes also absorbed by palladium. Portions of each of the pure gases were then brought into the eudiometer and exploded, the oxygen being in excess in some and the hydrogen in other experiments. As soon as a large volume of the gases had been brought into combination by successive

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[1] *Phil. Trans.* 1893, **184**, A, 543.

introductions followed by explosions, the residue remaining in the eudiometer was analysed and the amount of residual hydrogen or oxygen and impurity ascertained; this last was always extremely small, often less than 1/100,000 of the total volume, and probably contained nitrogen. This was then subtracted and the volumes of the two gases thus determined. The final result obtained from the whole series of 53 experiments was that at 15° 1 volume of oxygen unites with 2·00245 volumes of hydrogen, whilst at 0° the ratio is 1 : 2·00285. These gases, therefore, deviate from Gay-Lussac's law, according to which the volumes would be in the simple ratio 1 : 2, the strict accuracy of this generalisation, and of Avogadro's theory which is founded on it, being affected by the deviation of all gases from the laws of Boyle and Dalton. This deviation must of course vary with the pressure and temperature at which the comparison is made, since the two gases deviate to different extents from Boyle's law, and hence if Gay-Lussac's law were true for oxygen and hydrogen under one set of conditions, it would cease to be strictly true when the conditions were altered.

Morley, after first of all[1] arriving at the ratio 1 : 2·0002 by experiments carried out by the eudiometric method, has finally[2] estimated the ratio in which the gases combine at 1 : 2·00269. This estimate is based on the determination of the density of the electrolytic gas obtained from dilute caustic soda solution, which had been freed from carbon dioxide by the addition of baryta, a correction being made for a slight excess of hydrogen which was invariably found. From the known densities of the separate gases and from their known deviations from the gas laws the volumes of the two gases in the mixture were then calculated and the ratio thus ascertained.

Similar experiments carried out by Leduc[3] gave the ratio 1 : 2·0037.

151 A convenient form of voltameter for demonstrating the composition of water by volume is shown in Fig. 74. On passing a current of electricity through the water, acidified with sulphuric acid, which fills the U-shaped tube, bubbles of oxygen rise from the surface of the platinum plate forming the positive pole (anode), whilst bubbles of hydrogen are disengaged from the

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[1] *Amer. J. Science*, 1891, **41**, 220; *Chem. News*, 1891, **63**, 218.

[2] Smithsonian Contributions to Knowledge, 1895, *Zeit. physikal. Chem.* 1896, **20**, 417.

[3] *Compt. rend.* 1892, **115**, 41.

negative pole (cathode). The gases from each pole are collected separately, and the volume which collects in the tube containing the negative pole is seen to be a little more than double that which collects from the positive pole. On trial the latter is found to be oxygen, and the former hydrogen. In this experiment the volume of the oxygen gas is found to be rather less than half that of the hydrogen, because, in the first place, it is more soluble in water than hydrogen, and, secondly, because a portion of the oxygen is converted into ozone, which, being condensed oxygen, occupies a less volume than oxygen in the ordinary form. The fact that ozone is thus produced may be shown by bringing some iodised starch paper in contact with the electrolytic gas, when iodine will be liberated, and the paper will at once be turned blue. By raising the temperature of the acidulated water to 100°, the solution of the gases is prevented, and at the same time the formation of ozone is avoided, so that the true volume relation is thus much more closely attained.

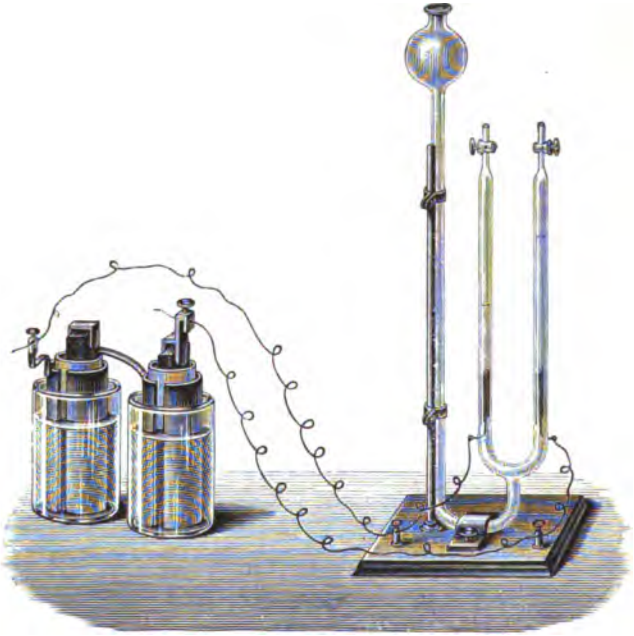

Fig. 74.

It must be remembered that the decomposition of the water is not directly caused by the passage of the electric current.

The sulphuric acid which is present yields the ions $\overset{+}{H},\overset{+}{H}$ and $\overset{--}{SO_4}$ (p. 119), the former of which give up their charges of electricity at the negative pole and escape from the solution, the atoms combining to form molecules of hydrogen. The ions $\overset{--}{SO_4}$, on the other hand, give up their charges at the positive pole and at once decompose, oxygen being liberated and a fresh quantity of sulphuric acid formed:—

$$SO_4 + H_2O = H_2SO_4 + O.$$

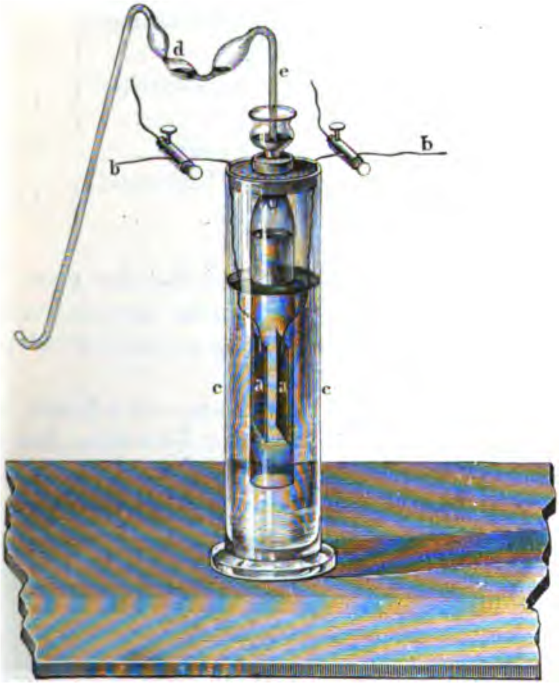

FIG. 75.

The atoms of oxygen then unite to form molecules which escape from the solution, whilst the regenerated sulphuric acid again undergoes a similar series of changes.

The apparatus, of which the construction is plainly shown in Fig. 75, is used for collecting the mixed gases evolved by the electrolysis of water. The mixed gases, thus prepared, combine with explosive violence when a flame is brought in contact with them, or when an electric spark is passed through the mixture.

In this act of combination, the whole of the hydrogen and the whole of the oxygen unite to form water: in other words, subject to the correction above referred to respecting the volume of water formed, the total volume of the detonating gas disappears. That this is the case is seen from the following experiments made by Bunsen, in which air was mixed with the electrolytic gas, the mixture exploded, and then the volume of air determined. A second addition of the explosive gas was next made and the volume of air again read off, and the operation repeated a third time.[1]

Original volume of air, in which detonating gas had been once exploded.	112·68
After explosion, with 55·19 vols. detonating gas	112·68
Ditto, measured again after 24 hours . .	112·57
After second explosion with 71·23 vols. detonating gas.	112·66

As already mentioned Morley found that the gases obtained by the electrolysis of pure caustic soda solution contained a slight excess of hydrogen, amounting to about 0·029 per cent. of the whole volume of gas.

152 *Volumetric Composition of Steam.*—Gay-Lussac not only determined the composition of water by volume, but was the first to ascertain that three volumes of the mixed gases combine to form two volumes of gaseous steam; inasmuch as he found the specific gravity of steam to be 0·6235, the number deduced from the above reaction being 0·6221.

This fact can be readily shown by exploding some of the electrolytic detonating gas evolved from the voltameter, Fig. 75, in the eudiometer E, Fig. 76, which is so arranged that the pressure on the gas can be altered at pleasure. Surrounding the eudiometer is a glass tube (T), and between the two tubes a current of the vapour of amyl alcohol, which boils at 132°, is passed from the flask (F), the vapour, after passing through the tube, being condensed in the flask cooled in the trough of water (H). When the temperature of the tube and of the gas has risen to 132°, the volume of the gas is exactly read off on the divided scale of the eudiometer; the height of the mercury in the two limbs having been brought up to the same level by

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[1] *Gasometry*, p. 65.

means of the reservoir of mercury (M) attached to the iron foot of the eudiometer by the indiarubber tube (G). The pressure on the gas is now reduced by lowering the level of the mercury

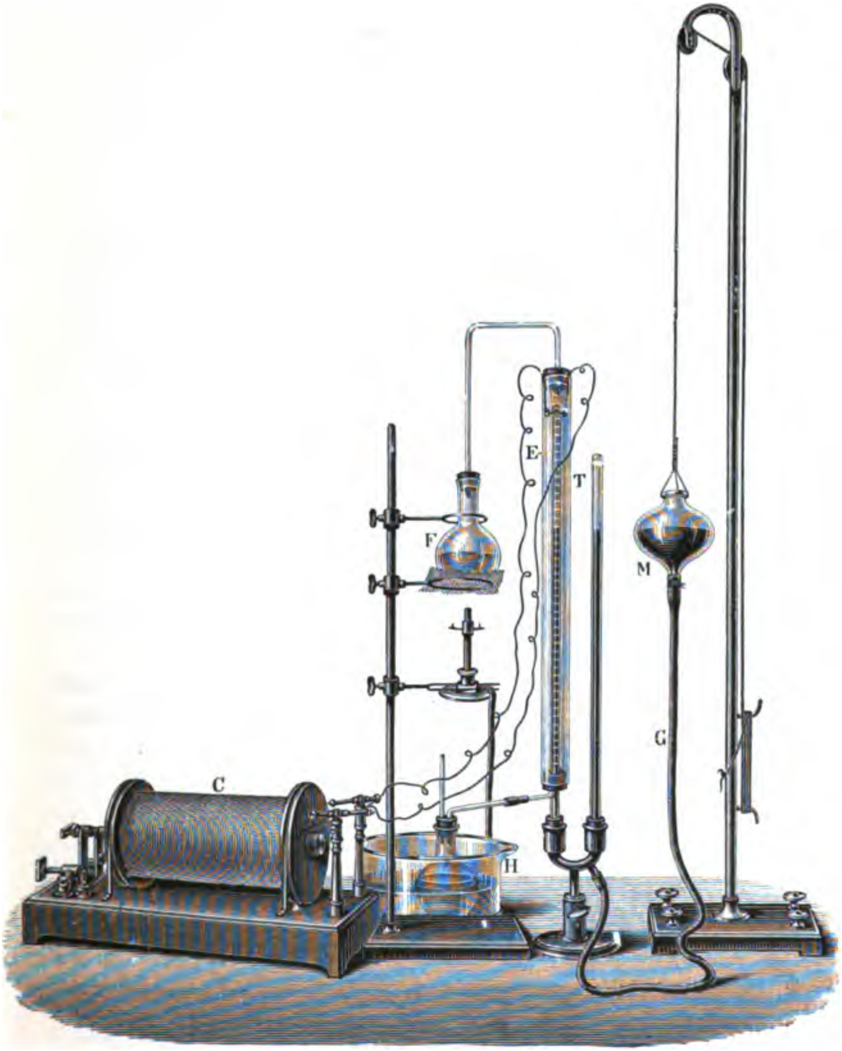

Fig. 76.

and, by means of the induction coil (C), a spark is passed. As soon as combination has taken place, the level of mercury in the two tubes is brought to the same height, and the volume of the gaseous water is accurately read off, the temperature of the whole being still kept up to 132° by the current of amyl alcohol vapour. This volume is found to be almost exactly two-thirds of that of the original mixed gases, and hence we conclude that 2 vols. of hydrogen and 1 vol. of oxygen unite together to form 2 vols. of steam or gaseous water.

The Composition of Water and the Atomic Weight of Oxygen.

153 A knowledge of the composition of water by weight is of the utmost importance, because the ratio in which hydrogen and oxygen combine must be known before the exact atomic weight of the latter (hydrogen being taken as the unit) can be determined. The earlier experimenters adopted a very simple method for this purpose.

Many metallic oxides such as copper oxide, CuO, when heated in a current of hydrogen lose their oxygen, which combines with the hydrogen to form water, the metal being produced. By ascertaining the loss of weight which the oxide thus suffers, and by weighing the water formed, we obtain all the data required for determining the ratio by weight in which the two gases are present in water, inasmuch as water contains no other constituent besides oxygen and hydrogen.

This method of determining the synthesis of water by weight was first proposed and carried out in 1819 by Berzelius and Dulong,[1] with the following results:—

Synthesis of Water by Weight (Berzelius and Dulong).

No.	Loss of weight of copper oxide.	Weight of water obtained.	Percentage Composition of water.	
			Oxygen.	Hydrogen.
1	8·051	9·052	88·942	11·058
2	10·832	12·197	88·809	11·191
3	8·246	9·270	88·954	11·046

It is thus seen that the separate experiments do not agree very closely among themselves, and do not, therefore, yield us certain information as to the exact proportions by weight in which

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[1] *Ann. Chim. Phys.* 1819, [2], **15**, 386.

the gases combine to form water. The atomic weight of oxygen derived from the totals of oxygen used and of water formed is 16·00.

In the year 1842 Dumas[1] undertook in conjunction with Stas, a most careful repetition of these experiments; pointing out the following probable sources of error in Berzelius's experiments :—

(1) The weight of water formed ought either to be ascertained *in vacuo* or reduced to a vacuum ; this reduction would increase the quantity of water by about 10 to 12 milligrams.

(2) The weight of oxygen ought also to be reduced to a vacuum.

(3) The hydrogen ought to be much more carefully dried than was the case in the older experiments.

(4) Lastly, even supposing that the weights had thus been adjusted, and if the hydrogen had been properly dried, Berzelius's determinations were made upon too small a scale to ensure the necessary degree of accuracy.

A facsimile of the apparatus used by Dumas is shown in Fig. 77.

The hydrogen, evolved from zinc and sulphuric acid in F may contain sulphur dioxide, arsine, sulphuretted hydrogen, traces of carbon dioxide, and moisture. In order to remove these it is passed successively over broken glass moistened with lead nitrate to remove the sulphuretted hydrogen, over silver sulphate to decompose arsine, through a number of tubes containing pumice moistened with caustic potash, and solid potash alone to remove carbon dioxide and sulphur dioxide, and finally through two tubes filled with phosphoric oxide and placed in a freezing mixture to dry the gas thoroughly, so that the gas passing through the stop-cock *r* into the bulb B consists of perfectly dry and pure hydrogen. In order to render this certain, the small tube next to the bulb is weighed before and after the experiment, and if its weight remain constant we have proof that the gas has been properly dried. In some of the experiments sulphuric acid was also used as a drying agent.

The copper oxide, which must be very carefully dried by heating, since it is hygroscopic, is contained in the bulb B, blown on hard glass, and is connected with B_1, a second bulb in which the water formed in the experiment collects. The last traces of water are absorbed in the next two tubes containing potash and

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[1] *Compt. rend.* 1842, **14**, 537 ; *Ann. Chim. Phys.* 1843, [3], **8**, 189.

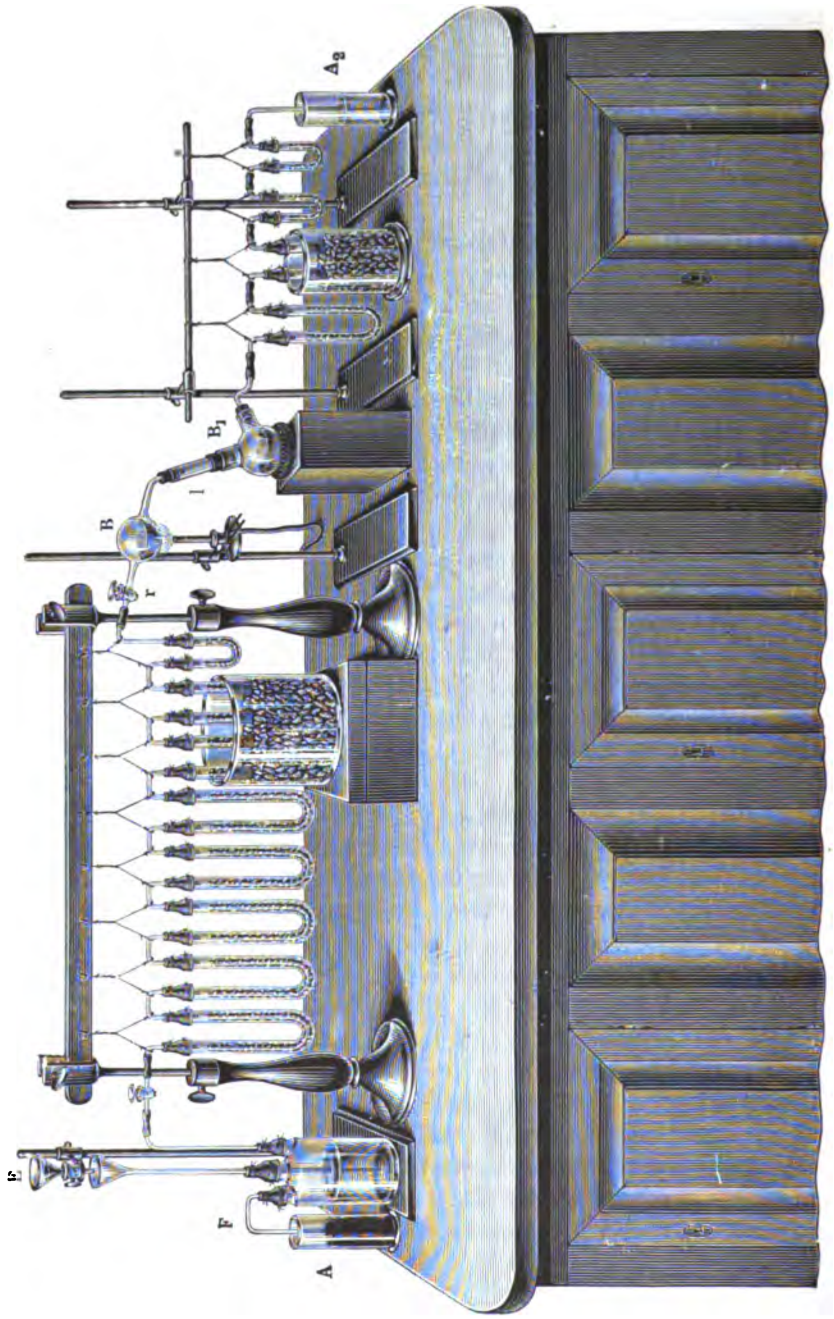

Fig. 77.

phosphoric oxide respectively. Next to these is placed a small weighed tube containing phosphoric oxide, whilst at the end we find another tube like the last, but not weighed. A cylinder A_2 filled with sulphuric acid, through which the excess of hydrogen gas escapes, completes the arrangement.

With this apparatus Dumas made no less than 19 separate experiments carried out with very great care.

The bulb containing the oxide is evacuated and its weight accurately determined, and after all the air has been driven out of the U-tubes by the dry hydrogen, the bulb is fixed in its place. The bulb destined to receive the water is also carefully weighed before the experiment, together with the 3 drying-tubes placed beyond it. Then the oxide of copper is heated to dull redness; the reduction commences, and the formation of water continues for from 10 to 12 hours. After this, the bulb B is allowed to cool in a current of hydrogen; the apparatus is then taken to pieces, the bulb rendered vacuous and weighed, whilst the hydrogen contained in the bulb and tubes serving to collect the water is displaced by dry air before this portion of the apparatus is weighed. It is clear that the weight of hydrogen is not directly determined by this method, but that it is obtained as the difference between the weight of water produced, and that of the oxygen consumed. As, however, the weight of the hydrogen is only $\frac{1}{9}$ of that of the water formed, it is evident that a percentage error of a given amount on the weight of water will represent a much larger percentage error on the smaller weight of hydrogen obtained by difference. The simplest way of reducing such errors is to arrange the experiment so that a large quantity of water is obtained, for the experimental errors remain, for the most part, constant, and by increasing the quantity of substance experimented upon, the percentage error is kept down. For this purpose Dumas took such weights of copper oxide as would produce in general about 50 grams of water, and succeeded in reducing the experimental error, on hydrogen taken as the unit, to 0·005 of its weight. In the 19 experiments Dumas found that 840·161 grams of oxygen were consumed in the production of 945·439 grams of water; or the percentage composition of water by weight is as follows :—

Percentage Composition of Water by Weight (Dumas).

Oxygen	88·864
Hydrogen	11·136
	100·000

In other words two parts by weight of hydrogen combine with 15·9608 parts by weight of oxygen to form water.

This number, which was almost simultaneously confirmed by Erdmann and Marchand,[1] using the same method, is in almost exact accordance with the results of the volumetric analysis of Bunsen, and the density determinations of Regnault. According to the former, the ratio of the volumes in which the two gases combine is exactly 1 : 2, whilst the latter found that oxygen is 15·96 times as heavy as hydrogen.

Dumas' results represented the most accurate determinations made before the year 1888, but since that time a number of investigations on the subject has been made with the utmost care and accuracy, the result of which has been to show that the number 15·96 is undoubtedly too high. The chief sources of error in the experiments of Dumas are—(1) the presence of impurities in the hydrogen; (2) the fact that heated copper takes up a certain amount of hydrogen, forming a hydride of this metal; (3) the action of the hydrogen upon sulphuric acid, used by Dumas in some of his experiments as a drying agent, by which sulphur dioxide is liberated.

In the more recent determinations, the results of which are given in the table on p. 284, these errors have as far as possible been avoided. Thus Cooke and Richards, Noyes and Keiser, weighed the hydrogen employed, the last-named in the form of palladium hydride, the others as the free gas, together with the water produced by the reduction of copper oxide. Dittmar and Henderson, and Leduc made use of Dumas' original method, whilst Rayleigh weighed both the hydrogen and the oxygen, but not the water.

The most recent and probably the most accurate work on this subject consists of a highly elaborate and painstaking series of researches which has been carried out by Morley,[2] who has made three independent determinations of the atomic

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[1] *J. pr. Chem.* 1842, **26**, 468.

[2] Smithsonian Contributions to Knowledge, 1895; *Zeit. physikal. Chem.* 1896, **20**, 68, 242, 417.

weight of oxygen, all of which have resulted in the same number, 15·88. The first of these determinations is based on the relative densities of the gases and the proportion by volume in which they combine, the values employed being 15·9002 for the relative density of oxygen and 1 : 2·00269 for the ratio of the combining volumes.

The second and third determinations were carried out by effecting a complete gravimetric synthesis of water, the hydrogen, the oxygen and the water produced from them being all weighed. The hydrogen, about 3·8 grams (42 litres) of which were required for a single experiment, was absorbed by 600 grams of palladium, and the amount used was ascertained by the loss of weight of the palladium tube after the gas had been driven off by heat. The oxygen was prepared by heating dried pure potassium chlorate and was weighed in two large balloons, the united capacity of which amounted to about 21 litres, the loss of weight during the experiment giving the amount of the gas employed. The gases were brought by tubes of glass ending in platinum into a special form of eudiometer, which had previously been evacuated. The apparatus was cooled by water and the combustion was started by a spark and continued until the pressure of the gases was too low for a flame to be produced. The residual gas was then removed by the pump and analysed, the amounts of hydrogen and oxygen thus found being subtracted from those of the two gases determined by weighing, and allowance was made for the small amounts of nitrogen, averaging about 0·006 c.c. per litre, and for the carbon dioxide, derived from asbestos plugs of the drying tubes, which was occasionally found to be present. The weight of water produced was ascertained by weighing the eudiometer before and after the combustion. In this way, as the mean of 11 experiments, the atomic weight of oxygen was found from the ratio by weight of hydrogen to oxygen to be 1 : 15·8792, and from the ratio of hydrogen to water to be 1 : 15·8785.

It may, therefore, be concluded that two parts by weight of hydrogen combine with 15·88 of oxygen to form 17·88 parts of water, the percentage composition of which is the following :—

Hydrogen	11·186
Oxygen	88·814
	100·000

The following table contains a summary of the results obtained by the different investigators who have determined the relative atomic weights, density and combining volumes of these two elements:—

Name.	Date.	Atomic Weight.	Density.	Combining Volumes.
Gay-Lussac and Humboldt	1805	...	...	1 : 2
Berzelius and Dulong [1]	1819	16·00		
Dumas	1842	15·961		
Erdmann and Marchand [2]	1842	15·96		
Regnault	1845	...	15·96	
Regnault [3] corrected	...	...	15·91	
Rayleigh [4]	1882	...	15·884	
Cooke and Richards [5]	1888	15·869		
Keiser [6]	1888	15·950		
Rayleigh [4]	1889	15·89		
Noyes [7]	1890	15·897		
Dittmar and Henderson [8]	1890	15·866		
Morley [9]	1891	15·879	...	1 : 2·00023
Leduc [10]	1891	...	15·905	1 : 2·0037
Rayleigh [4]	1892	...	15·882	
Leduc [10]	1892	15·881		
Scott [11]	1893	...		1 : 2·00245
Morley [12]	1895	15·88	15·9002	1 : 2·00269

Experiments with the Detonating Mixture of Oxygen and Hydrogen.

154 In order to exhibit the explosive force of this detonating gas a thin bulb (B), Fig. 78, of a capacity from 70 to 100 cubic centimetres is blown on a glass tube. This is filled with the gas evolved from the voltameter (A) as shown in the figure, and,

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[1] Berzelius and Dulong, *Ann. Chim. Phys.* 1819, [2], **15**, 386.

[2] Erdmann and Marchand, *J. pr. Chem.* 1842, **26**, 468.

[3] Regnault (corrected by Crafts), *Compt. rend.* 1888, **106**, 1662.

[4] Rayleigh, *Proc. Roy. Soc.* **43**, 356; **45**, 425; **50**, 448.

[5] Cooke and Richards, *Amer. Chem. Journ.* 1888, **10**, 81, 191.

[6] Keiser, *Amer. Chem. Journ.* 1888, **10**, 249.

[7] Noyes, *Amer. Chem. Journ.* 1890, **12**, 441.

[8] Dittmar and Henderson, *Proc. of Glasgow Phil. Soc.* 1890–91; *Chem. News*, 1893, 54.

[9] Morley, *Amer. Journ. of Science*, 1891, [3], **41**, 220; *Chem. News*, 1891, **63**, 218, &c.

[10] Leduc, *Compt. rend.* 1891, **113**, 186; 1892, **115**, 41, 311; 1893, **116**, 1248.

[11] Scott, *Phil. Trans.* 1893, **184**, A, 543.

[12] Morley, Smithsonian Contributions to Knowledge, 1895; *Zeit. physikal. Chem.* 1896, **20**, 68, 242, 417.

when full, is placed over the perforated cork (C), through which two insulated copper wires are inserted, these being connected at the extremity by a fine platinum wire. The bulb is then surrounded with a protecting cover of wire gauze (G), and a current of electricity passed through the platinum wire, which soon becomes heated to a temperature high enough to cause an instantaneous combination of the oxygen and hydrogen to occur; a sharp explosion is heard, and the bulb is shattered to fine dust.

The amount of the energy thus generated can be easily calculated when the quantity of heat developed by the combination is known. Thus 1 gram of hydrogen on burning to form water evolves 33,970 thermal units, or heat sufficient to raise 33,970 grams of water from 0° to 1°. But the mechanical equivalent of heat is 423, that is, a weight of 423 grams falling through the space of 1 metre is capable of evolving heat enough to raise 1 gram of water from 0° to 1°. Hence 1 gram of hydrogen on burning to form water, sets free an amount of energy represented by that required to raise a weight of 33,970 × 423 grams or 14,309 kilograms through the space of 1 metre.

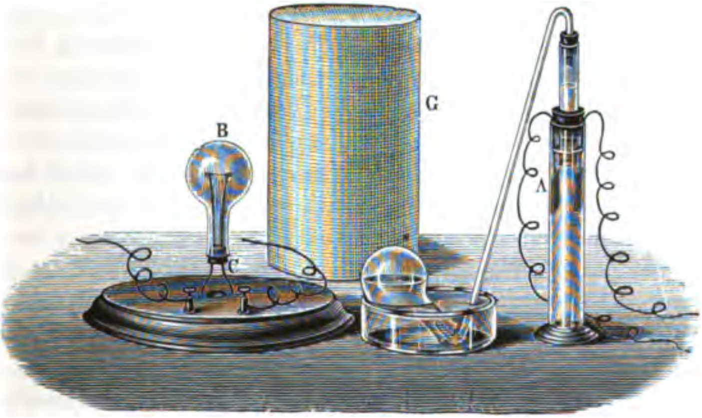

FIG. 78.

The gases may, however, be made to combine not only rapidly, as we have seen, but also slowly and quietly. High temperature, the passage of the electric spark, and the presence of platinum and other bodies effect the change in the first of these ways. The smallest electric spark suffices to cause the combination of the largest masses of pure detonating gas, because the heat which is evolved by the union of those particles in whose neighbourhood the spark passes is sufficient to cause the combination of the adjacent particles, and so on. In every case a certain minimum temperature, termed the *temperature of ignition,* differing for each gas, must be reached in order that the union shall take place, and the temperature may be so lowered by mixing the detonating gas in certain proportions with inactive gases that the explosive mixture cannot inflame. Thus one volume of detonating gas explodes when mixed with 2·82 vols. of carbon dioxide, with 3·37 vols. of hydrogen, or with 9·35 vols. of oxygen: but it does not explode when mixed with 2·89 vols. of carbon dioxide, with 3·93 vols. of hydrogen, or with 10·68 vols. of oxygen.[1]

When the mixture of electrolytic gases is sealed up in a glass bulb (which can be done without explosion occurring if the side tubes are of capillary bore) and heated in the vapour of boiling sulphur (448°) combination begins to take place slowly, the whole of the mixed gases being at length converted into water without any explosion occurring. If on the other hand the bulb be immersed in the vapour of boiling zinc chloride (606°) an explosion invariably takes place. This does not occur, however, until the temperature reaches 650—730° if the gas is passed through the bulb in a slow stream. The temperature at which combination commences is much influenced by the nature of the surface with which the gas is in contact. Thus if the interior of the bulb be coated with silver, combination begins at as low a temperature as 155°.[2]

The phenomena which occur when detonating gas is heated depend very largely on the purity of the gas and are greatly influenced by the presence of moisture. The gases obtained by the electrolysis of an aqueous solution of pure barium hydrate, appear to be quite free from hydrocarbons as well as from ozone and hydrogen peroxide, and in fact represent the purest form of detonating gas that has hitherto been prepared. When these gases are confined in a well-cleaned hard glass tube, and very thoroughly dried by prolonged exposure to purified phosphoric oxide, they do not explode or combine when the tube is

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[1] Bunsen, *Gasometry*, p. 248.

[2] V. Meyer and Krause, *Annalen*, 1891, **264**, 85; V. Meyer and Askenasy, *Annalen*, 1892, **269**, 49; V. Meyer and Freyer, *Ber.* 1892, **25**, 622; *Zeit. physikal. Chem.* 1893, **11**, 28; V. Meyer, *Ber.* 1891, **24**, 4233. See also Mitscherlich, *Ber.* 1893, **26**, 160.

heated to redness, and a silver wire may be melted in them (960·5°) without any combination occurring. On the other hand a platinum wire brings about explosive combination when heated to just visible redness. When only partially dried, the gases slowly unite when heated, and, although visible water is present, no explosion takes place.

A further remarkable property of the detonating gas prepared as described above is that the undried gases unite slowly when exposed to sunlight at the ordinary temperature, but not in the dark. The dried gases do not unite at the ordinary temperature either in the light or in the dark.[1]

The following experiments indicate the slow combination of oxygen and hydrogen. If a spiral of clean platinum wire is held for a few seconds in the flame of a Bunsen burner, and then the flame extinguished and the gas still allowed to stream out round the spiral, it will be seen that the spiral soon becomes red hot, either continuing to glow as long as the supply of gas is kept up, or rising to a temperature sufficient to ignite the gas (Davy). A palladium wire acts in a similar way, but wires of gold, silver, copper, iron and zinc produce no action of this kind.

A perfectly clean surface of platinum plate also first effects a slow, but after a time even an explosive combination of the detonating gas (Faraday). The finely-divided metal (spongy platinum) which exposes a great surface to the action of the gas, also induces, at the ordinary temperature, the combination of hydrogen with air or oxygen; at first a slow combustion takes place, but when the metal becomes red hot, a sudden explosion occurs (Döbereiner).

Small traces of certain absorbable gases, such as ammonia, destroy the inflaming power of the spongy platinum, but this power is regained on ignition. The most probable explanation of this property of platinum is that this metal possesses the power of condensing on to its surface a film of hydrogen and oxygen, which gases, when brought under these circumstances into intimate contact, are able to combine at the ordinary atmospheric temperature, and by the heat which their combination evolves, to excite the union of the remaining gaseous mixture.

The following experiment strikingly shows that a mixture of hydrogen and air becomes inflammable only when a definite proportion between the two gases has been reached. Fig. 79

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[1] Baker, *Journ. Chem. Soc.* 1902, **81**, 400.

represents a suspended glass bell-jar closed at the top, and covered at its mouth by a sheet of paper gummed on to the glass. A glass syphon passing through the paper cover is fastened by copper wires to the bell-jar with the longer limb on the outside. By means of a gas-generating apparatus the bell-jar is filled with hydrogen by displacement, a rapid current of the gas being made to pass in through the syphon, the air finding its way out through the pores of the paper. When the bell-jar is full of hydrogen, the vulcanised tube is removed from the end of the long limb of the syphon, and the stream of hydrogen gas which issues from the end (hydrogen, being lighter than the air, can be syphoned upwards) is then lighted and is seen to burn with its usual quiet non-luminous flame. After a short time, however, this flame may be seen to flicker, and is heard to emit a musical note which begins by being shrill, but gradually deepens to a bass sound, until, after a time, distinct and separate

FIG. 79.

impulses or beats are heard, and at last, when the requisite proportion between the hydrogen and the air which enters through the pores of the paper has been reached, the flame is seen to pass down the syphon and enter the bell-jar, when the whole mass ignites with a sudden and violent detonation.

155 *The Phenomena of Explosion in Gases.*—The phenomena which accompany the ignition of a detonating gas are of a very interesting and important character. Bunsen, who was the first to investigate this subject, directed his attention mainly to two points, the rate of propagation of the explosion and the pressure produced, both of which have been more fully studied by later investigators.[1]

Bunsen,[2] in 1867, attempted to determine the rate at which the explosion is propagated by igniting the gas as it issued from the end of a narrow tube and measuring the rate at which the detonating mixture had to be supplied to prevent the flame passing back along the tube. In this way he found for hydrogen and oxygen the rate of 34 metres per second.

In 1881, however, it was observed that when the explosive gas is fired in a tube, the rate of explosion increases from its origin until it reaches a certain maximum, after which it remains constant whatever the length of the column of gas may be (Berthelot, Mallard and Le Chatelier). The disturbance by which the ignition is propagated throughout the gas is known as the "explosion wave"; the maximum rate attained is exceedingly high and has a perfectly definite and constant value for each explosive mixture. The experiment of Bunsen, as will be seen, referred to the initial period of the combination before the explosion wave had attained its characteristic velocity.

In order to determine the rate, the detonating gas is brought into a leaden tube, about 9 mm. in diameter and 100 metres in length, which is closed at either end by steel stop-cocks. Near one end the gas can be fired by means of an electric spark, and at about four feet from this point an insulated bridge of silver foil is placed across the interior of the tube, a second similar bridge being placed near the second stop-cock. These bridges convey electric currents, and are connected with a delicate chronograph. The gas is fired by a spark, and the explosion,

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[1] Berthelot, "Sur la Force des Matières Explosives (Paris)," *Ann. Chim. Phys.* 1883, [5], **28**, 289; Mallard and Le Chatelier, *Compt. Rend.* 1881, **93**, 145; 1900, **130**, 1755, "Combustions des Mélanges Gazeux"; Dixon, *Phil. Trans.* 1893, **184**, 97; 1903, A. **200**, 315.

[2] *Phil. Mag.* 1867, [4], **34**, 493.

after attaining its maximum rate in the first four feet of the tube, breaks the first bridge, passes throughout the length of the tube, and finally breaks the second bridge, the time which elapses between the two ruptures being recorded by the chronograph. In the case of hydrogen and oxygen the enormous velocity of 2,821 metres per second has been found, and the rates in other gases are of the same order of magnitude.

The addition of an excess of one or other of the gases or of an inert gas is found to modify the rate of explosion by altering the temperature which is attained and the density of the gases. Thus, in a mixture of 8 vols. of hydrogen with 1 of oxygen the rate is 3,532 m., whilst in one containing 1 vol. of hydrogen with 3 vols. of oxygen it is 1,707 m. per second. These velocities correspond closely with those which would be attained by *sound* in the gases concerned at the high temperature produced by the combustion under the circumstances of the experiment (Dixon). The ignition seems indeed to be propagated in somewhat the same manner as a sound-wave. The numbers calculated for hydrogen and oxygen on this supposition agree well with the experimental results obtained with the diluted gases. When the pure detonating gas is employed, however, the calculated results are invariably higher than the experimental. This is probably due to the fact, that a certain fraction of the gas escapes combustion in the explosion wave, the temperature of which is probably above that at which the dissociation of steam begins. The greater part of this uncombined gas undergoes combustion as a secondary reaction after the passage of the wave, but about 1 per cent. entirely escapes and is found in the tube at the close of the experiment (Dixon).

According to Bunsen's experiments the pressure produced when electrolytic gas is exploded is equal to 9·5 atmospheres, and a similar result was subsequently obtained by Berthelot. By comparing this result with the pressure as calculated from the heat of combination, Bunsen concluded that only one-third of the total volume of gas is burnt at the highest temperature of the explosion. Later experiments made with more delicate appliances have shown that the pressures produced in the explosion wave, although of exceedingly short duration, are considerably higher in value than those measured by Bunsen; the pressure in the case of electrolytic gas for example probably exceeds 20 atmospheres.

156 *The Oxyhydrogen Flame.*—By bringing a jet of oxygen

gas within a flame of hydrogen gas, burning from a platinum nozzle, a flame of the mixed gases is obtained which evolves but very little light, although it possesses a very high temperature. A watch-spring held in the flame quickly burns with bright scintillations. Platinum, one of the most infusible of the metals, can be readily melted and even boiled, whilst silver can thus be distilled without difficulty.

Fig. 80.

The arrangement of such an oxyhydrogen blowpipe is seen in Fig. 80, the gases being collected separately in the two gasholders. The nozzle at S (Fig. 81) is screwed on to the tap of the oxygen gasholder, the points *a* and *b* serving to keep the oxygen tube in the centre, whilst the hydrogen enters the tube

Fig. 81.

by the opening W, which is connected with the supply of this gas by a caoutchouc tube. The hydrogen is first turned on and ignited where it issues from the point of the nozzle; the oxygen tap is then gently turned on so that the flame burns quietly. No backward rush of gas or explosion can here occur, for the gases only mix at the point where combustion takes place.

If any solid, infusible, and non-volatile substance, such as a piece of quick-lime, be held in the flame, the temperature of the surface of the solid is raised to a very high point and an intense white light is emitted, which is frequently used, under the name of the Drummond light, for illuminating purposes.

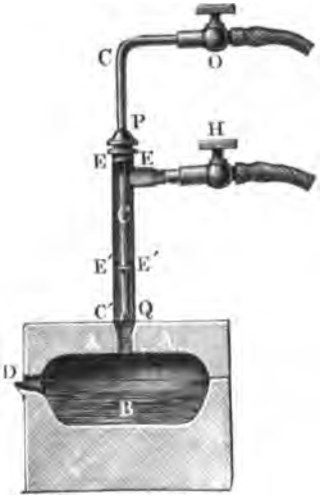

FIG. 82.

In certain metallurgical processes, especially in working the platinum metals, this high temperature of the oxyhydrogen flame is turned to useful account. One of the forms of furnace used for this purpose is shown in Fig. 82. It is built from a block of very carefully burnt lime A, A, which has been cut in half and then each piece hollowed out, so that when brought together they form a chamber into which the substance to be melted is placed. The upper block is perforated to allow the nozzle (C′, Q) of the blowpipe to fit in, and the gases pass from the separate gasholders, into two concentric tubes C C and

E′ E′, each provided with a stop-cock (O and H), the hydrogen being delivered by the outer and the oxygen by the inner tube. MM. Deville and Debray[1] in this way melted 50 kilos. of platinum in one operation, and Messrs. Johnson, Matthey & Co. melted, by this process, a mass of pure platinum weighing 100 kilos., which was shown at the Exhibition of 1862. At a later date the same firm melted no less than 250 kilos. of an alloy of platinum and iridium for the International Metrical Commission.

The oxyhydrogen flame as a means of production of high temperatures has now been in many cases superseded by the electric furnace.

PROPERTIES OF WATER.

157 Pure water is a clear, tasteless liquid, colourless when seen in moderate quantity, but when viewed in bulk possessing a bluish green colour, well seen in the water of certain springs, especially those in Iceland, and in certain lakes, particularly those of Switzerland, which are fed by glacier streams. This blue colour is also observed if a bright white object be viewed through a column of distilled water about six to eight metres in length, contained in a tube with blackened sides and plate-glass ends. Water is an almost incompressible fluid, one million volumes becoming less by fifty volumes when the atmospheric pressure is doubled; it is a bad conductor of heat, and, like all pure liquids, has a very low electrical conductivity, its value being probably $0·04 \times 10^{-6}$.

Expansion and Contraction of Water.—When heated from 0° to 4°, water is found to *contract*, thus forming a striking exception to the general law, that bodies expand when heated and contract on cooling; on cooling from 4° to 0° it *expands* again. Above 4°, however, it follows the ordinary law, expanding when heated, and contracting when cooled. This peculiarity in the expansion and contraction of water may be expressed by saying that *the point of maximum density of water is* 4° C.; or according to the exact determinations of Joule, 3°·945: that is, a given bulk of water will at this temperature weigh more than at any other. Although the amount of

[1] *Ann. Chim. Phys.* 1859 [3], **56**, 385.

contraction on heating from 0° to 4° is but small, yet it exerts a most important influence upon the economy of nature. If it were not for this apparently unimportant property, our climate would be perfectly Arctic, and Europe would in all probability be as uninhabitable as Melville Island. In order better to understand what the state of things would be if water followed the ordinary laws of expansion by heat, we may perform the following experiment, first made by Dr. Hope. Take a jar containing water at a temperature above 4°, place one thermometer at the top and another at the bottom of the liquid. Now bring the jar into a place where the temperature is below the freezing point, and observe the temperature at the top and bottom of the liquid as it cools. It will be seen that at first the upper thermometer always indicates a higher temperature than the lower one; after a short time both thermometers mark 4°; and, as the water cools still further, it will be seen that the thermometer at the top always indicates a lower temperature than that shown by the one at the bottom: hence we conclude that water above or below 4° is lighter than water at 4°. This cooling goes on till the temperature of the top layer of water sinks to 0°, after which a crust of ice is formed; and if the mass of the water be sufficiently large, the temperature of the water at the bottom is never reduced below 4°. In nature precisely the same phenomenon occurs in the freezing of lakes and rivers;[1] the surface-water is gradually cooled by cold winds, and thus becoming heavier, sinks, whilst lighter and warmer water rises to supply its place: this goes on till the temperature of the whole mass is reduced to 4°, after which the surface-water never sinks, however much it be cooled, as it is always lighter than the deeper water at 4°. Hence ice is formed only at the top, the mass of water retaining the temperature of 4°. Had water become heavier as it cooled down to the freezing point, a continual circulation would be kept up, until the mass was cooled throughout to 0°, when solidification of the whole would ensue. Thus our lakes and rivers would be converted into solid masses of ice, which the summer's warmth would be quite insufficient thoroughly to melt; and hence the climate of our now temperate zone might approach in severity that of the Arctic regions.

The following table gives the volume and specific gravities

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[1] The point of maximum density of sea-water is considerably lower than that of fresh water, and is in fact below 0° C.

of water for temperatures varying from 0° to 100°, according to the most accurate experiments.[1]

Temperature.	Volume.	Specific Gravity.	Temperature.	Volume.	Specific Gravity.
0°	1·000122	0·999878	19°	1·00153	0·99847
1	1·000067	0·999933	20	1·00173	0·99827
2	1·000028	0·999972	21	1·00194	0·99806
3	1·000007	0·999993	22	1·00216	0·99785
4	1·000000	1·000000	23	1·00238	0·99762
5	1·000008	0·999992	24	1·00262	0·99739
6	1·000031	0·999969	25	1·00287	0·99714
7	1·000067	0·999933	30	1·00425	0·99577
8	1·000118	0·999882	35	1·00586	0·99417
9	1·000181	0·999819	40	1·00770	0·99236
10	1·000261	0·999739	45	1·00974	0·99035
11	1·000350	0·999650	50	1·01197	0·98817
12	1·000456	0·999544	55	1·01436	0·98584
13	1·000570	0·999430	60	1·01694	0·98334
14	1·000703	0·999297	65	1·01967	0·98071
15	1·000847	0·999154	70	1·02261	0·97789
16	1·000997	0·999004	80	1·02891	0·97190
17	1·001162	0·998839	90	1·03574	0·96549
18	1·001339	0·998663	100	1·04323	0·95856

158 *Latent Heat of Water.*—In the passage from solid ice to liquid water, we notice that a very remarkable absorption or disappearance of heat occurs. This is rendered plain by the following simple experiment:—Let us take a kilogram of water at the temperature 0°, and another kilogram of water at 79°. If we mix these, the temperature of the mixture will be the mean, or 39°·5; if, however, we take one kilogram of ice at 0° and mix it with a kilogram of water at 79°, we shall find that the whole of the ice is melted, but that the temperature of the resulting 2 kilograms of water is exactly 0°. In other words, the whole of the heat lost by the hot water has just sufficed to melt the ice, but has not raised the temperature of the water thus produced. Hence we see that in passing from the solid to the liquid state a given weight of water takes up or *renders latent* just so much heat as would suffice to raise the temperature of the same weight of water through 79° C.; the *latent heat of water*

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[1] Volkmann, *Wied. Ann.* 1881, **14**, 260.

is, therefore, said to be 79 *thermal units*—a thermal unit meaning the *amount of heat required to raise a unit weight of water through* 1° C. When water freezes, or becomes solid, this amount of heat, which is necessary to keep the water in the liquid form, and is, therefore, well termed the *heat of liquidity*, is evolved, or rendered sensible. A similar disappearance of heat on passing from the solid to the liquid state, and a similar evolution of heat on passing from the liquid to the solid form, occurs with all substances ; the amount of heat thus evolved or rendered latent varies, however, with the nature of the substance. A simple means of showing that heat is evolved on solidification consists in obtaining a saturated hot solution of sodium acetate, and allowing it to cool. Whilst it remains undisturbed, it retains the liquid form, but if agitated, it at once begins to crystallise, and in a few moments becomes a solid mass. If a delicate thermometer be now plunged into the salt while solidifying, a rapid rise of temperature will be noticed.

159 *Freezing Point of Water and Melting Point of Ice.*—Although water usually freezes at 0° it was observed so long ago as 1714 by Fahrenheit that under certain circumstances water may remain liquid at temperatures much below this point. Thus, when brought under a diminished atmospheric pressure, water may be cooled to $-12°$ without freezing: or if water be boiled in a glass flask, and the neck of the flask be plugged whilst it is hot with cotton wool, the flask and its contents may be cooled to $-9°$ without the water freezing; but when the cotton wool is taken out, particles of dust fall into the water, and these bring about an immediate crystallisation, the temperature of the mass quickly rising to 0°. Sorby[1] has shown that when contained in thin capillary glass tubes, water may be cooled to $-15°$ without freezing, whilst Boussingault[2] has exposed water contained in a closed steel cylinder to a temperature of $-24°$ for several days in succession without its freezing. The melting point of ice under the ordinary atmospheric pressure is 0°, but this point is lowered by increase of pressure ; thus under a pressure of 8·1 atmospheres, ice melts at $-0°{\cdot}059$, and under 16·8 atmospheres at $-0°{\cdot}129$, or the melting point is lowered by about $0°{\cdot}0075$[3] for every additional atmosphere. This peculiarity of a lowering of the melting point

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[1] *Phil. Mag.* 1854 [4], **18**, 105.

[2] *Compt. Rend.* 1871, **73**, 77.

[3] James Thomson, *Edin. Roy. Soc. Trans.* 1849, **16**, 575

under pressure is common to all substances which, like water, expand in passing from the liquid to the solid state, whilst in the case of bodies which contract under like circumstances, the melting point is raised by increase of pressure. Thus Bunsen in the case of paraffin,[1] and Hopkins in the case of sulphur, obtained the following results:—

Under a pressure of 1 atmosphere, paraffin melts at 46°·3
„ „ 85 „ „ 48°·9
„ „ 100 „ „ 49°·9
„ „ 1 atmosphere, sulphur melts at 107°·0
„ „ 519 „ „ 135°·2
„ „ 792 „ „ 140°·5

From what has been stated we should expect that by increasing the pressure upon ice it could be melted, and Mousson [2] has shown that this is the case, for by exposing it to a pressure of 13,000 atmospheres he has converted ice into water at a temperature of $-18°$. This lowering of the melting point of ice with pressure explains the fact that when two pieces of ice are rubbed together the pressure causes the ice to melt at the portions of the surface in contact, the water thus formed running away, and the temperature being lowered; then as soon as the excess of pressure is taken away the two surfaces freeze together at a temperature below 0°, one mass of solid ice being produced. This phenomenon, termed *regelation*, was first observed by Faraday in 1850, and was afterwards applied by Tyndall to explain glacier motion.

160 The crystalline form of ice is hexagonal, being that of a rhombohedron. Snow crystals exhibit this hexagonal form very clearly; they usually consist of crystals which have grown on to another crystal in the direction of the three horizontal axes, so that the snow crystal clearly exhibits these three directions, as shown in Figs. 83, 84.

Ice is transparent, and when seen in small quantities it appears to be colourless, though large masses of ice, such as icebergs or glaciers, possess a deep blue colour; like water it is also a bad conductor of heat and of electricity, and becomes electrified when rubbed.

Water on freezing increases nearly $\frac{1}{11}$ of its bulk, or, according

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[1] *Ann. Chim. Phys.* 1852 [3], **35**, 383

[2] *Pogg. Ann.* 1858, **105**, 161.

to the exact experiments of Bunsen,[1] the specific gravity of ice at 0° is 0·91674, that of water at 0° being taken as the unit; or one volume of water at 0° becomes 1·09082 volumes of ice at the same temperature. This expansion plays an important part in the disintegration and splitting of rocks during the winter. Water penetrates into the cracks and crevices of the rocks, and on freezing widens these openings; this process being repeated over and over again, the rock is ultimately split into fragments. Hollow balls of thick cast-iron can thus easily be split in two by filling them with water and closing by a tightly fitting screw, and then exposing them to a temperature below 0°.

FIG. 83.

FIG. 84.

161 *Latent Heat of Steam.*—Under the normal barometric pressure of 760 mm. water boils in a metal vessel at 100° C. When liquid water is converted into gaseous steam, a large quantity of heat becomes latent, the temperature of the steam given off being the same as that of the boiling water. The amount of ***heat latent in steam*** is roughly ascertained by the following experiment. Into 1 kilogram of water at 0°, steam from boiling water, having the temperature of 100°, is passed until the water boils: it is then found that the whole weighs 1·187 kilos., or 0·187 kilo. of water in the form of steam at 100° has raised 1 kilo. of water from 0° to 100°; or 1 kilo. of steam at 100° would raise 5·36 kilos. of ice-cold water through 100°, or 536

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[1] *Phil. Mag.* 1871, [4], **41**, 165.

kilos. through 1°. Hence the *latent heat of steam is said to be* 536 *thermal units.*

Whenever water evaporates or passes into the gaseous state, heat is absorbed, and so much heat may be thus abstracted from water that it may be made to freeze by its own evaporation. A beautiful illustration of this is found in an instrument called Wollaston's Cryophorus, Fig. 85; it consists of a bent tube, having a bulb on each end, and containing water and vapour of water, but no air. On placing all the water in one bulb, and plunging the *empty* bulb into a freezing mixture, a condensation of the vapour of water in this empty bulb occurs, and a corresponding quantity of water evaporates from the other bulb to supply the place of the condensed vapour; this condensation and evaporation go on so rapidly that in a short time the water cools down below 0°, and a solid mass of ice is left in the bulb. By a very ingenious arrangement this plan of freezing water by its own evaporation has been practically carried out by Carré, by means of which ice can be most easily prepared. This arrangement consists simply of a powerful air-pump (A, Fig. 86), and a reservoir (B) of a hygroscopic substance such as strong sulphuric acid. On placing a bottle of water (C) in connection with this apparatus, and pumping for a few minutes, the water begins to boil rapidly, and its temperature is so lowered by the evaporation that the water freezes to a mass of ice.

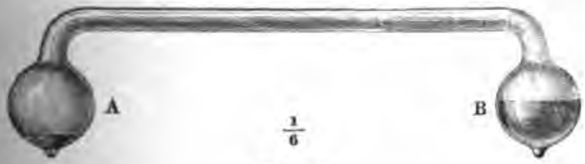

FIG. 85.

162 *Pressure of Aqueous Vapour.*—Water, and even ice, constantly gives off steam or aqueous vapour at all temperatures, when exposed to the air. Thus we know that if a glass of water be left in a room for some days, the whole of the water will gradually evaporate. This power of water to rise in vapour at all temperatures is due to the *elastic force* or *pressure* of aqueous vapour; it may be measured, when a small quantity of water is placed above the mercury in a barometer, by the extent to which the vapour thus given off is capable of

depressing the mercurial column. If we gradually heat the drops of water thus placed in the barometer, we shall notice that the column of mercury gradually sinks; and when the water is heated up to 100° C., the mercury in the barometer tube is found to stand at the same level as that in the trough, showing that the elastic force of the vapour at that temperature is equal to the atmospheric pressure. *Water is said to boil in the air when the pressure of its vapour is equal to the superincumbent atmospheric pressure.* On the tops of mountains, where the atmospheric pressure is less than at the sea's level, water boils at a temperature below 100°: thus at Quito, at a height of 2,914 metres above the sea's level, the mean height of the barometer is 523 mm., and the boiling point of water is 90°·1; that is, the pressure of aqueous vapour at 90°·1 is equal to the pressure exerted by a column of mercury 523 mm. high. Founded on this principle, an instrument has been constructed for determining heights by noticing the temperatures at which water boils. A simple experiment to illustrate this fact consists in boiling water in a globular flask, into the neck of which a stop-cock is fitted: as soon as the air is expelled, the stop-cock is closed, and the flask removed from the source of heat; the boiling then ceases; but on immersing the flask in cold water, the ebullition recommences briskly, owing to the reduction of the pressure consequent upon the condensation of the steam—the pressure of the vapour at the temperature of the water in

FIG. 86.

the flask being greater than the diminished pressure. All other liquids follow a similar law respecting ebullition; but as the pressures of their vapours are very different, their boiling points vary considerably.

When steam is heated alone, it expands according to the law previously given for permanent gases; but when water is present, and the experiment is performed in a closed vessel, the elastic force of the steam increases in a far more rapid ratio than the increase of temperature. The following table gives the pressure of aqueous vapour, as determined by experiment, at different temperatures measured on the air thermometer.

Table of the Pressure of the Vapour of Water.

Temperature Centigrade.	Pressure in millimetres of mercury.	Temperature Centigrade.	Pressure in atmosphs., 1 atmosphere = 760 mm. of mercury.
−20°	0·927	100°	1
−10	2·093	111·7	1·5
0	4·600	120·6	2
+ 5	6·534	127·8	2·5
10	9·165	133·9	3
15	12·699	144·0	4
20	17·391	159·2	6
30	31·548	170·8	8
40	54·906	180·3	10
50	91·982	188·4	12
60	148·791	195·5	14
70	233·093	201·9	16
80	354·280	207·7	18
90	525·450	213·0	20
100	760·000	224·7	25

163 *Water as a Solvent.*—Water is the most generally valuable of known solvents. Not only do many solids, such as sugar and salt, dissolve in water, but certain liquids, such as alcohol and acetic acid, mix with it completely. Other liquids again, such as ether, dissolve to a certain extent in water, although they do not mix with it in all proportions. Gases also dissolve in water, some, such as ammonia and hydrochloric acid, in very large quantities, exceeding more than one hundred times the bulk of the water; others, again, such as hydrogen and nitrogen,

are but very slightly soluble, while carbon dioxide and some other gases stand, as regards solubility, between these extremes.

Concerning the nature of solution, whether of solids, liquids, or gases, we know at present but little. The phenomena of solution differ, however, essentially from those of chemical combination, inasmuch as in the former we have to do with gradual increase up to a given limit, termed the *point of saturation*, whereas in the latter we observe the occurrence of a limited number of constant proportions in which, and in no others, combination occurs. Solution follows a law of continuity, chemical combination one of sudden change or discontinuity.

The solubility of solids varies with the essential nature of the solid, with that of the liquid, and with the temperature at which they are brought together; the same may be said of the solvent action of water upon liquids and upon gases, except that the solubility of gases is also influenced by the pressure to which the gas and the water are subjected. The quantity of any solid, liquid, or gas which dissolves in a solvent, such as water, must be ascertained empirically in every case, as we are unacquainted with any law according to which such solvent action takes place, and we therefore cannot calculate the amount. The effect of change of temperature on the solubility of a substance, whether solid, liquid, or gaseous, must likewise be determined by experiment, but the effect of pressure upon the solubility of gases is given by a simple law, known as the law of Dalton and Henry (p. 306).

The solubility of most solids increases with the temperature, a limit being reached at each temperature, beyond which no further quantity of the solid dissolves. When the temperature of such a saturated solution falls, or when the solvent is allowed to evaporate, a portion of the dissolved substance is deposited from solution, usually in the form of a solid possessing some definite geometrical form and termed a *crystal*, whilst the substance is said to *crystallise*.

164 *Water of Crystallisation.*—Many salts owe their crystalline character to the presence in a solid state of a certain definite number of molecules of water. When this chemically combined water is driven off by heat, the crystal falls to powder, and hence it has been termed water of crystallisation. Some salts contain a large quantity of water definitely combined in this form; thus the opaque white powder of anhydrous alum,

$K_2Al_2(SO_4)_4$, unites with no less than twenty-four molecules of water to form the well-known transparent octohedral crystals of common alum, $K_2Al_2(SO_4)_4 + 24H_2O$; in like manner anhydrous and powdery sodium carbonate, Na_2CO_3, when dissolved in water, deposits large monoclinic crystals of common washing-soda, having the composition $Na_2CO_3 + 10H_2O$. The temperature of the solution from which such crystals are deposited materially affects the quantity of water with which the salt combines; thus, in the case of sodium carbonate, whilst monoclinic crystals of the ten-molecule hydrate are deposited at the ordinary temperature, other crystals, having the composition $Na_2CO_3 + 7H_2O$, or again others represented by the formula $Na_2CO_3 + 5H_2O$, are deposited when crystallisation is allowed to take place at higher temperatures.

The water in these crystals has a definite vapour pressure and is, therefore, given off when the temperature becomes so high that the pressure of the water of crystallisation is greater than that in the surrounding atmosphere. Different substances lose their water in the air at very different temperatures, and even the molecules of water combined with a single molecule of salt behave differently in this respect. Thus potash alum loses ten molecules of water at 100°, but it needs to be heated to 120° in order to drive off a second ten molecules of water, and retains the last four molecules until the temperature rises to 200°. Copper sulphate in a similar manner loses four of its molecules of water below 110°, whilst the fifth is only driven off at 200°. Sodium carbonate, $Na_2CO_3 + 10H_2O$, loses water on simple exposure to the air, the pressure of its combined water being as a rule greater than that of the aqueous vapour in the atmosphere, and the salt becomes covered with a white powder. Crystals which behave in this manner are said to *effloresce*. Many salts which do not lose water in the atmosphere do so when placed in dry air. Other solid salts, such as calcium chloride and potassium acetate, combine with water with such avidity that when left exposed to the air they begin to liquefy from absorption of the atmospheric moisture; the salts are then said to *deliquesce*.

In the year 1840 Dalton observed that different salts, whose water of crystallisation has been driven off by heat, dissolve in water without increasing the volume of the liquid, whereas if the hydrated salt is dissolved, an increase of volume occurs which is exactly that due to the water which is combined in the salt. Playfair and Joule[1] extended these observations, showing, for

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[1] *Chem. Soc. Mem.* **2**, 477; **3**, 54, 199; *Journ. Chem. Soc.* 1849, **1**, 121.

instance, that in the case of sodium carbonate, crystallising with ten molecules of water, and in that of the phosphates and arsenates, crystallising with twelve molecules, the volume of the whole molecule of hydrated salt is the same as that of its water of crystallisation would be if frozen to ice. The particles of anhydrous salt would hence appear to occupy the spaces intervening between those of the water without increasing its volume. Thus the crystals of common washing soda have the following composition:

$$
\begin{array}{lr}
Na_2CO_3 \; . \; . \; . \; . \; . = & 105·31 \\
10H_2O \; . \; . \; . \; . \; . = & 178·80 \\
\hline
 & 284·11
\end{array}
$$

and 284·11 grams. of these crystals occupy exactly the space of 178·8 grams. of ice.

The following table gives the specific gravities of the abovementioned salts, first as observed by experiment, and secondly as calculated upon the above hypothesis, and shows the close agreement of the two sets of numbers.

		Specific Gravity.	
		Observed.	Calculated.
Sodium Carbonate	$Na_2CO_3 + 10\ H_2O$	1·454	1·463
Hydrogen Sodium Phosphate	$Na_2HPO_4 + 12\ H_2O$	1·525	1·527
Normal Sodium Phosphate	$Na_3PO_4 + 12\ H_2O$	1·622	1·622
Hydrogen Sodium Arsenate	$Na_2HAsO_4 + 12\ H_2O$.	1·736	1·736
Normal Sodium Arsenate	$Na_3AsO_4 + 12\ H_2O$	1·804	1·834

In the case of certain other salts the volume of the crystal was found to be equal to the sum of the volume of the water when frozen and that of the anhydrous salt.

165 *Cryohydrates.*—It has been already mentioned that when a dilute solution is cooled, ice separates out (p. 117). If the ice be removed and the cooling continued, a temperature is at length reached at which the whole solution becomes solid. Thus Guthrie,[1] who has investigated this subject, found that when a dilute solution of common salt is cooled down to $-1°·5$, ice begins to separate out, and this formation of ice continues until the temperature sinks to $-23°$, at which the whole mass becomes solid. A concentrated salt solution, on the other hand, deposits at $-7°$ crystals having the composition $NaCl + 2H_2O$, and the separation of this compound, in the form of iridescent

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[1] *Phil. Mag.* 1875, [4], 49, 1, 206, 266.

scales, also goes on until the liquid has cooled down to −23°, when, as before, it freezes *en masse.*

The solid mass thus formed has been called a *cryohydrate*, and resembles a chemical compound inasmuch as it has a definite composition and a definite melting-point. It has, however, been shown that these so-called cryohydrates are simply mixtures of ice and a solid salt, and that their properties are in all cases the mean of those of their constituents.[1]

166 *Freezing Mixtures.*—The solution of a solid in water is generally accompanied by a lowering of temperature, caused by the conversion of sensible into latent heat by the liquefaction of the solid. In the case, however, of many anhydrous salts, solution is accompanied by a rise in temperature, which may possibly be caused by the production of a definite chemical compound between the solid and the solvent. By the solution of many salts such a diminution of temperature is effected that this process may be used for obtaining ice; thus when 500 grams of potassium thiocyanate are dissolved in 400 grams of cold water, the temperature of the solution sinks to − 20°. When common salt is mixed with snow or pounded ice, a considerable reduction of the temperature of the mass occurs, the two solid bodies becoming liquid and forming a concentrated brine whose freezing-point lies at − 23°. This solution contains thirty-two parts by weight of salt to 100 parts of water, and in order to bring about the greatest possible reduction in temperature the salt and snow must be mixed in the above proportions. Equal weights of crystallised calcium chloride and snow when mixed together give a freezing mixture whose temperature sinks from 0° to − 45°.

The temperatures attainable in this way are those at which the so-called cryohydrates are formed, since these are the lowest temperatures at which the mass can remain liquid.

167 *Absorption of Gases by Water.*—All gases are soluble to a greater or less degree in water, the extent of this solubility depending upon (1) the nature of the gas, (2) the temperature of the gas and water, (3) the pressure under which the absorption occurs. No simple law is known expressing the relation between the amount of gas absorbed and the temperature. Usually the solubility of a gas diminishes as the temperature increases, but the rate of diminution varies with each gas, so that the amount

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[1] Offer, *Wien. Akad. Ber.* **81**, ii, 1058; see Findlay, *The Phase Rule* (Longmans, 1904), p. 115.

of gas dissolved in water at a given temperature can be ascertained only by experiment. A simple relation has however been found to exist between the quantity of the same gas absorbed under varying conditions of pressure, the temperature remaining constant.

In the year 1803 William Henry[1] proved that the amount of gas absorbed by water varies directly as the pressure, or, in the words of the discoverer of the law, "under equal circumstances of temperature, water takes up in all cases the same *volume* of condensed gas as of gas under ordinary pressure. But as the spaces occupied by every gas are inversely as the compressing force, it follows that water takes up of gas condensed by one, two, or more additional atmospheres, a quantity which ordinarily compressed would be equal to twice, thrice, and so on, the volume absorbed under the common pressure of the atmosphere." Two years after Henry had enunciated this law, Dalton[2] extended the law to the case of mixed gases, proving that when a mixture of two or more gases in given proportions is shaken up with water, the volume of the gas having a finite relation to that of the liquid, the absorptiometric equilibrium occurs when the pressure of each gas dissolved in the liquid is equal to that of the portion of the gas which remains unabsorbed by the liquid; the amount of each gas absorbed by water from such a mixture being solely dependent on the pressure exerted by the particular gas. This law, termed *Dalton's law of partial pressures*, may be illustrated by the following example: if two or more gases which do not act chemically upon each other be mixed together, and the mixture of gases brought into contact with water until the absorptiometric equilibrium is established, the quantity of each gas which dissolves is exactly what it would have been if only the one gas had been present in the space. Thus, for instance, the *absorption co-efficient* of oxygen at 0° is 0·04890, that of nitrogen at the same temperature being 0·023481. Now 100 volumes of air contain on an average 79·04 volumes of nitrogen and 20·96 volumes of oxygen, hence the partial pressure of the oxygen is 0·2096 of an atmosphere, whilst that of the nitrogen is 0·7904, and as the solubility of each gas is proportioned to its partial pressure,

$$0{\cdot}2096 \times 0{\cdot}04890 = 0{\cdot}010244$$

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[1] *Phil. Trans.* 1803, **29**, 274.

[2] *Manc. Memoirs*, 1805.

will be the proportion of oxygen dissolved, and

$$0{\cdot}7904 \times 0{\cdot}023481 = 0{\cdot}018559$$

will be the proportion of the nitrogen dissolved, or the percentage composition of the air dissolved in water will be:—

	Calculated.	Found.
Nitrogen	64·4	64·9
Oxygen	35·6	35·1
	100·0	100·0

Thus the relation between the dissolved gases as found by experiment agrees closely with that calculated on the above assumption, and the law of partial pressures is verified.

Every absorbed gas which follows the law of pressure will of course be driven out of solution when the pressure on the gas is reduced to zero. This can be effected by removing the superincumbent pressure by means of an air-pump, by allowing the liquid to come in contact with a very large volume of some other indifferent gas, or, lastly, by boiling the liquid, when all the dissolved gas will be driven off with the issuing steam, except where a chemical combination or attraction exists between the gas and the water.

Some gases dissolve in water in very large quantities, whereas others are only slightly soluble. Two distinct methods of experimentation are needed for ascertaining the co-efficients of solubility of these two classes. On the one hand, the amount of the absorbed gas is determined chemically; on the other, the volume of gas absorbed by a known volume of water is ascertained either by measuring the diminution in bulk of a given volume of the gas when agitated with water, or by saturating water with the gas and driving out the latter by heat and then measuring it. The first of these methods was that adopted by Bunsen,[1] to whom we are indebted for the first exact and extended experimental investigation of this subject. Among the gases whose solubility has been determined by chemical methods are oxygen, sulphuretted hydrogen, sulphur dioxide, ammonia, carbon dioxide, hydrochloric acid, and chlorine. These gases, evolved in a state of purity, were passed for a long time through a large volume of water, which

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[1] *Gasometry*, p. 129, or Watts's *Dictionary* (1st Edition), article "Gases, Absorption of, by Liquids."

had been freed from air by continued boiling, and was kept at a constant temperature during the experiment. After the gas had passed so long through the water that the latter was completely saturated, the barometric pressure was read off, and a known volume of the water withdrawn, special precautions to avoid possible loss of the gas being observed. The gas contained in this liquid was then quantitatively determined either by means of volumetric analysis, or by the ordinary processes of analytical chemistry. If the volume of the liquid does not undergo any appreciable alteration in bulk owing to the absorption of the gas, we are easily able to calculate the co-efficients of absorption from the data obtained by this process. If, however, the volume of the saturated liquid is considerably larger, as is usually the case, than that of the liquid before saturation, either the specific gravity of the saturated liquid must be ascertained, or only a small volume of water must be saturated, and the absolute quantity of absorbed gas ascertained by weighing before and after the experiment.

168 Bunsen's *Absorptiometer*, as shown in Fig. 87,[1] consists essentially of two parts: (1) a eudiometric tube, *e*, in which a measured volume of the gas to be experimented upon is brought in contact with a given volume of water; (2) an outer vessel, consisting of a glass cylinder, fitting at the lower end into a wooden stand, *f*, and having a water-tight lid at the upper end. The eudiometer tube, which is divided and accurately calibrated, is partially filled with the given gas in the usual way over a mercurial trough, and the volume of this gas read off with all due precautions; a measured volume of water perfectly free from air is next admitted under the mercury into the tube, and the open end of the tube then closed by screwing it tightly against the caoutchouc plate of the small iron foot, *a*, fixed on to its lower end, as shown in Fig. 88. The tube by this means can be removed from the mercurial trough, without any danger of losing gas or water, and placed in the glass cylinder, which contains mercury *a* in its lower part, and water above, in which it can be safely shaken to ensure the establishment of the proper absorptiometric equilibrium between gas and water. The pressure in the tube can be readily adjusted from time to time by unscrewing the open ends of the tube from the caoutchouc plate, and thus placing the mercury inside in connection with that outside the tube. The heights of the two

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[1] *Bunsen's Gasom.* 43 and 44

levels of mercury and the level of the water in the tube, as well as the temperature (indicated by the thermometer *k*), can then

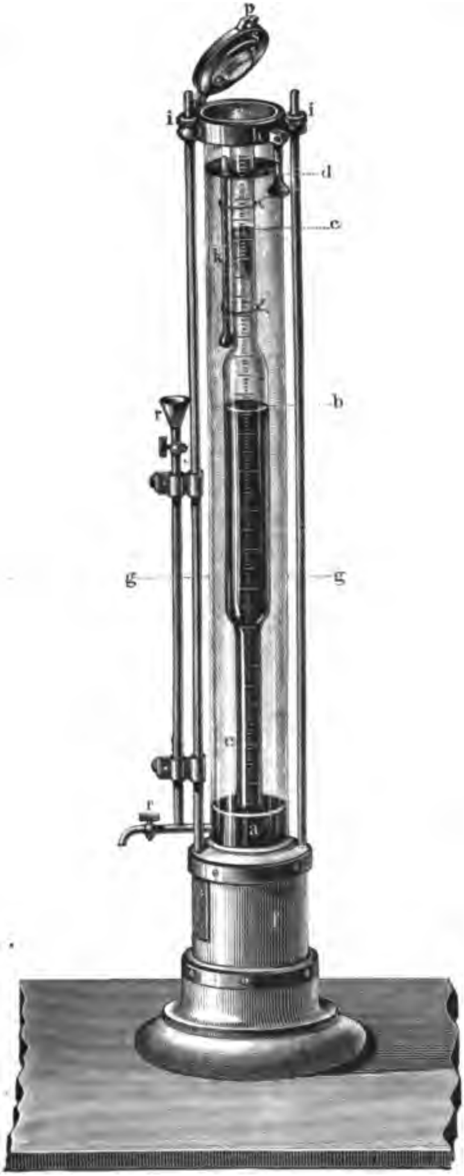

Fig. 87.

Fig. 88.

be read off through the glass cylinder, and thus all the data are obtained for ascertaining exactly the volume of gas absorbed by a given volume of water under given conditions of temperature and pressure.

Still more accurate results have been obtained by the use of various modified forms of this apparatus, in which larger volumes of water are employed.[1]

169 The truth of the law of Dalton for pressures not greatly higher than that of the atmosphere has been experimentally tested by Bunsen,[2] who showed that the results of an absorptiometric analysis of a gaseous mixture—that is, of an experimental determination of its solubility in water, from which the composition of the original gaseous mixture is calculated, on the supposition that the law of partial pressures holds good—agrees exactly with a direct eudiometric analysis of the same mixture. Thus it has been shown by the same chemist that in mixtures of carbon dioxide and carbon monoxide, of carbon monoxide and marsh gas, of carbon dioxide and hydrogen, the component gases are absorbed in quantities exactly corresponding to Dalton's law.

The limits of pressure beyond which gases do not follow the law of pressures have not as yet been experimentally ascertained in many cases; but, at any rate in the case of the more soluble gases, the limits are reached within ranges of pressure varying from 0 to 2 atmospheres. That under high pressures deviations from the law must in many cases occur is clear, inasmuch as gases do not conform to the law of Boyle under greatly increased pressure. So too, it is found that certain gases which follow the law of absorption at one temperature do not conform at another; thus, for instance, ammonia dissolves in water at 100° under high pressures, in quantities exactly proportional to the pressure, although at lower temperatures this is not the case.[3]

Instances also occur in which certain gases, although agreeing with the law of pressures when in the pure state, do not follow it when mixed together with other gases. Thus, in mixtures of equal volumes of chlorine and hydrogen, and mixtures of varying proportions of chlorine and carbon dioxide, the carbon dioxide and hydrogen do not dissolve in water in quantities proportional to their partial pressures, although they both follow the law when unmixed with other gases.[4] (See p. 185.)

Amongst the various applications of the laws of the absorption

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[1] Winkler, L. W. *Ber.* 1891, **24**, 89; Timofejew, *Zeit. physikal Chem.* 1890, **6**, 141.

[2] *Gasometry*, p. 124.

[3] Roscoe, *Journ. Chem. Soc.* 1856, 14.

[4] Sims, *Journ. Chem. Soc.* 1862, 1.

of gases in water none is more interesting than the process proposed by Mallet for solving the difficult problem of separating the atmospheric oxygen from the nitrogen. We have already seen that the percentage of oxygen contained in the air is 20·9, whereas the mixture of oxygen and nitrogen dissolved in water contains 35·1 per cent. of the former gas. If the gas thus dissolved be driven off by boiling, and then this again shaken up with water, the dissolved gases will possess about the following percentage composition :—

	After the second absorption.
Nitrogen	52·5
Oxygen	47·5
	100·0

This again set free, and again shaken up with water, yields a gaseous mixture, containing 75 per cent. of oxygen. Continuing this process of alternately absorbing and liberating the mixture of gases, the percentage of oxygen regularly rises, until after the 8th absorption the gas contains 97·3 per cent., or is nearly pure oxygen gas.

NATURAL WATERS.

170 None of the various forms of water met with in nature are free from certain impurities. These may be of two kinds: (1) Mechanically suspended impurities; (2) Soluble impurities. The first can be separated either by subsidence or by mechanical filtration; the latter cannot be thus got rid of from the water, but must be separated by distillation or by some chemical reaction.

Even rain- or snow-water collected in clean vessels contains in addition to the dissolved atmospheric gases traces of foreign bodies which are contained in the air either as dust or vapour, and no sooner does rain-water touch the earth than it at once takes up into solution certain soluble constituents of the portion of the earth's crust through which it percolates, thus gradually becoming more and more impure until it again reaches the ocean from which it had its origin.

171 *Purification of Water.*—The separation of suspended matter is effected on the small scale for laboratory purposes by filtration through porous paper placed in glass funnels, and on the large scale by employing filtering beds of sand and gravel.

The soluble constituents may be distinguished as (1) fixed, and (2) volatile constituents, and water can be obtained free from the first of these by the process of distillation, whilst the latter may come over with the steam, and therefore require the employment of other means. In order to obtain pure distilled water, spring- or rain-water is boiled in a vessel termed a still, (B) Fig. 89, so arranged that the escaping steam is condensed by passing through a cooled worm or tube made of block tin, platinum, or silver, but not of glass, for if this substance be used a trace of its more soluble constituents, the alkaline silicates, is always dissolved. This process frees the water from all non-volatile impurities, provided care has been taken to prevent any mechanical spirting of the liquid, but substances which are volatile will still be found in the distillate. Thus ordinary distilled water invariably contains ammonia, as may easily be proved by adding a few drops of *Nessler's* reagent. This consists of an alkaline solution of mercuric iodide in potassium iodide. If a few drops of this reagent be added to about 100 c.c. of ordinary distilled water contained in a cylindrical glass standing on a white plate, the water will be seen to attain a distinct yellowish tint if small amounts of ammonia or ammoniacal salts be present, whilst if larger quantities of ammonia be present a brown precipitate will be formed.

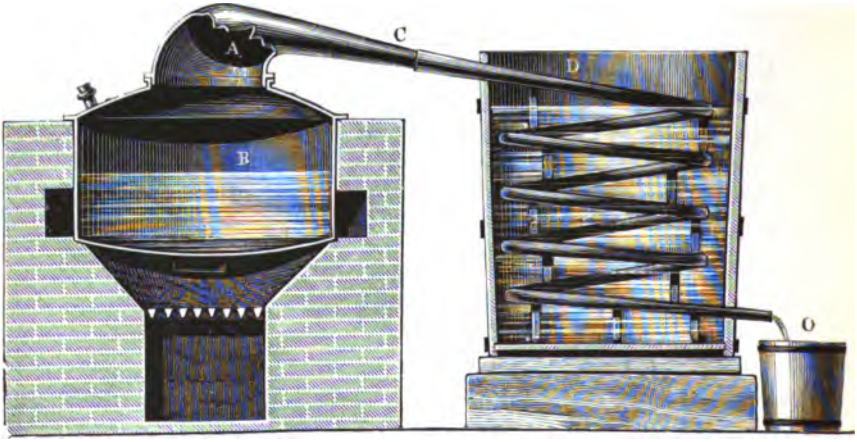

Fig. 89.

In order completely to free distilled water from volatile nitrogenous organic bodies which it is likewise apt to contain, it is necessary to re-distil it after solutions of potassium permanganate and caustic potash have been added. These substances oxidise the organic matter with formation of ammonia, and after about one-twentieth of the water has come over, the distillate is usually found to be free from ammonia, and to leave no residue on evaporation. If ammonia can be still detected the water must again be distilled with the addition of a small quantity of acid potassium sulphate, which fixes the ammonia.[1]

172 *Gases Dissolved in Water.*—All water contains in solution the gases of the atmosphere, oxygen, nitrogen, argon, and carbon dioxide. In order to obtain water free from these dissolved gases the water is well boiled, and the glass vessel in which it is boiled is then sealed hermetically. The arrangement Fig. 90 shows the apparatus used by Bunsen.[2] After the water has been quickly boiling for half an hour the indiarubber tube (*a*) from which the steam issues is closed by a clamp, the lamp is removed, and the drawn-out neck of the flask melted off before the blow pipe at (*b*).

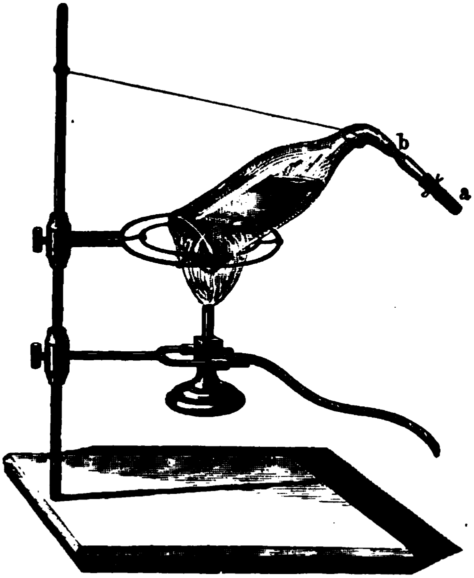

FIG. 90.

Even when boiled for many hours a small residue of nitrogen

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[1] Stas, *Recherches*, p. 109.

[2] *Gasometry*, p. 142.

gas is left behind, and on condensing, the steam coming off from such water leaves a minute bubble of nitrogen, so that it appears impossible in this way to obtain water quite free from nitrogen. All water which is exposed to the air dissolves a certain quantity of oxygen and nitrogen, a quantity which is determined by the laws of gas absorption. It is indeed upon this dissolved oxygen that the life of water-breathing animals depends. In every pure water the proportion between the dissolved nitrogen and oxygen is found to be constant at any given temperature, and it is represented at 10° by the following numbers:—

Percentage Composition of Air Dissolved in Water.

Oxygen	35·1
Nitrogen	64·9
	100·0

1,000 c.c. of pure water, such as rain-water, when saturated at 10°, dissolve 20·11 c.c. of air,[1] containing 7·87 c.c. of oxygen, and 14·50 c.c. of nitrogen, the ratio being 1 : 1·84 ; both the absolute amount and the composition of the dissolved gas vary with the temperature. If the water is rendered impure by the introduction of organic matter undergoing oxidation, the proportion between the dissolved oxygen and nitrogen becomes different owing to the oxygen having been partly or wholly used for the oxidation of this material. This is clearly shown in the analyses on page 315, made by Miller, of the dissolved gases contained in Thames water collected at various points above and below London.

This table shows that whereas the pure water at Kingston contained nearly the normal quantity of dissolved oxygen, the ratio of oxygen to nitrogen decreased at a very rapid rate as the river-water became contaminated with London sewage, but that this ratio again showed signs of a return to the normal at Erith.

Hence it is clear that an analysis of the gases dissolved in water may prove of some help in ascertaining whether the water is pure, or whether it has been contaminated with putrescent

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[1] Winkler, *Ber.* 1901, **34**, 140.

[2] Grove, *Journ. Chem. Soc.* 1863, 263.

organic matter. Indeed, Miller concludes that whenever the proportion between dissolved oxygen and nitrogen falls to less than 1 to 2 the water is unfit for drinking purposes. It is, however, found that oxygen is almost entirely absent from certain deep spring waters of great purity, although they contain their full complement of nitrogen.

In order to collect the gases dissolved in water, it is only necessary to boil the water and to collect in a suitable measuring apparatus the gases which thus become free. A simple form of apparatus used for this purpose is shown in Fig. 91. It consists of a globular flask, capable of holding from 500 to 1,000 c.c. of water. This flask, connected with a bulb and long tube by a strong piece of caoutchouc tubing, is filled with the water, the tubing being closed by a screw-clamp. The bulb, also containing water, is next heated so as to make the water boil briskly, and thus the air contained in the bulb and tube is driven out at the open end of the tube which dips under mercury. As soon as all the air is driven out, the screw-clamp is opened, and heat applied to the flask until the water boils, which under the diminished pressure it will soon do. The dissolved gases then begin to come off, and are collected and measured in the eudiometer filled with mercury, the operation being continued for not less than an hour, until the last trace of air has been expelled. A Geissler's mercury pump may also be employed for this same purpose, and the apparatus thus

—	Thames Water taken at					
	Kingston.	Hammersmith.	Somerset House.	Greenwich.	Woolwich.	Erith.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total volume of gas per litre .	52·7	—	62·9	71·25	63·05	74·3
Carbon dioxide.	30·3	—	45·2	55·6	48·3	57
Oxygen . . .	7·4	4·1	1·5	0·25	0·25	1·8
Nitrogen . . .	15·0	15·1	16·2	15·4	14·5	15·5
Ratio of oxygen to nitrogen. .	1 : 2	1 : 3·7	1 : 10·5	1 : 60	1 : 52	1 : 8·1

modified has been used for determining the amount of dissolved oxygen in water.[1]

The amount of oxygen dissolved in water may also be determined chemically by several methods,[2] the best of which depends upon a measurement of the amount of sodium hyposulphite which can be oxidised by a given volume of the water (Schützenberger).

173 The several kinds of naturally-occurring waters may be classed as rain-water, spring-water, river-water, and sea-water.

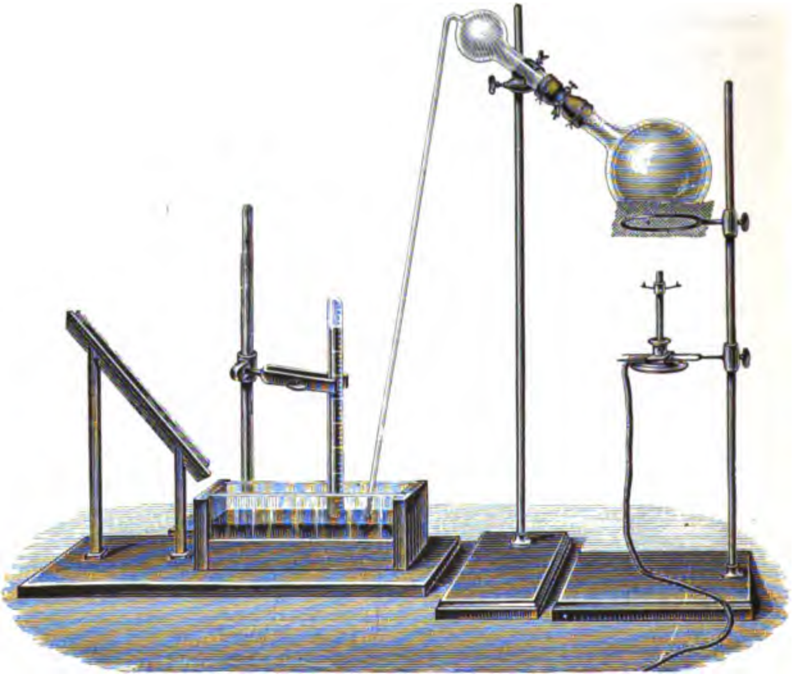

Fig. 91.

Rain-Water.—Although this is the purest form of natural water, inasmuch as it has not come into contact with the solid crust of the earth, it still contains certain impurities which are washed out by it from the atmosphere. Thus rain-water invariably contains ammoniacal salts, chloride of sodium, and organic matter of various kinds in the state of minute suspended

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[1] Roscoe and Lunt, *Journ. Chem. Soc.* 1889, 563.

[2] Roscoe and Lunt, *Journ. Chem. Soc.* 1889, 565; Thresh, *Journ. Chem. Soc.* 1890, 185.

particles which we see when a glass full of such water is held up to the light. The amount of the constituents thus taken out of the air by the falling rain may serve as a means of ascertaining the chemical climate of the locality, that is, the amount of those varying chemical constituents of the atmosphere which are brought in by local causes. Thus, for instance, the rain collected in towns where much coal is burnt is generally found to have an acid reaction, owing to the presence of free sulphuric acid derived from the oxidation of the sulphur contained in the pyrites present in most coal. The amount of this acid may reach, under certain circumstances, as much as 7 grains per gallon. In towns, the rain-water also contains a larger proportion of ammoniacal salts and nitrates than that falling in the country, whilst it is also found to hold in suspension or solution albuminous matter derived from decomposing animal substances. An elaborate examination of the chemical composition of a large number of samples of rain-water has been made by Angus Smith,[1] and in this work will be found not only a valuable series of original determinations of the constituents of rain-water collected in various parts of the country, but a statement of the results of the labours of other chemists on the same subject.[2]

According to the experiments of Lawes and Gilbert,[3] the average amount of nitrogen contained in country rain-water as ammonia, organic nitrogen, nitrous and nitric acids, is about 0·7 parts in a million of rain-water, whilst the rain of London (Hyde Park) contains 2·2 parts per million. Boussingault, on the other hand, found in the rain of Paris 4 parts of ammonia in one million, and of nitric acid 0·2 in a million.

Spring-Water.—The water flowing from springs, whether they are surface- or deep-springs, is always more impure than rain-water owing to the solution of certain portions of the earth's crust, through which the water has percolated. The nature and amount of the material taken up by the water must of course change with the nature of the strata through which it passes, and we accordingly find that the soluble constituents of spring-water vary most widely, some spring-waters containing only a trace of soluble ingredients, whilst others are highly charged with

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[1] *On Air and Rain: the Beginnings of a Chemical Climatology.* Longmans, 1872.

[2] See also Bailey, *Mem. Manc. Lit. and Phil.* 1894, [4], **8**, 11.

[3] *Sixth Report of the River Commissioners*, 1874.

mineral constituents. Those waters in which the soluble ingredients are present only in such proportion as not sensibly to affect the taste are termed *fresh waters;* whereas, those in which the saline or gaseous contents are present in quantity sufficient to impart to the water a peculiar taste or medicinal qualities are termed *mineral waters.* The salts which most commonly occur in solution in spring-water are: (1) The carbonates of calcium, magnesium, iron, and manganese, dissolved in an excess of carbonic acid. (2) The sulphates of calcium and magnesium. (3) Alkali carbonates, chlorides, sulphates, nitrates, or silicates. The gaseous constituents consist of oxygen, nitrogen, argon, and carbon dioxide; this last gas being present in varying amount though always in much larger quantity than we find it in rain-water. The nature and quantity of the inorganic as well as of the gaseous constituents of a fresh spring- or mineral-water must be ascertained by a complete chemical analysis, frequently a long and complicated operation.

174 *Mineral-Waters and Thermal Springs.*—Spring-waters which issue from considerable depths, or which originate in volcanic districts, are always hotter than the mean annual temperature of the locality where they come to the surface. In many of these springs the water issues together with a copious discharge of undissolved gas, and in some cases, as in the celebrated Geysers of Iceland, so carefully investigated by Bunsen,[1] steam accompanies the water or forces it out at certain intervals. Several remarkable hot-springs of this kind have been discovered in New Zealand, but a still more extensive series occurs in the district of the Yellowstone River in the United States. The following is a list of some important *thermal springs,* the temperature of all of which is much above that of the locality where they occur:—

THERMAL SPRINGS.

	Temp.		Temp.
Wildbad	37°·5	Baden-Baden	67°·5
Aachen . .	44° to 57°·5	Wiesbaden	70°
Vichy	45°	Karlsbad	75°
Bath	47°	Trincheras (Venezuela)	97°

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[1] On the Pseudo-Volcanic Phenomena of Iceland, *Cav. Soc. Memoirs,* 1848, p. 323.

The chief gases found free in these springs are carbonic acid and sulphuretted hydrogen.

According to the materials which the water contains in solution these springs may be grouped as follows:—

(1) *Carbonated Waters*, which are cold, and are rich in carbonic acid, and contain small quantities of alkali carbonates, chloride of sodium, and other salts. Amongst the best known of these are the waters of Seltzer, Apollinaris, and Taunus.

(2) *Alkaline Waters*, containing a larger quantity of sodium bicarbonate as well as common salt, and Glauber salt. These are sometimes warm, such as the springs at Ems and Vichy, but generally cold. They are often rich in carbonic acid.

(3) *Saline Waters* are those in which the alkali bicarbonate is replaced by other salts, thus *Glauber-salt water*, as Marienbad; *Magnesium water*, such as Friedrichshall, Seidschutz, and Epsom, in which the sulphate and chloride of magnesium occur; *Chalybeate waters*, in which ferrous carbonate is found dissolved in carbonic acid, such as those of Pyrmont and Spa; *Sulphuretted water*, containing sulphuretted hydrogen and the sulphides of the alkali metals, as the springs at Aachen and Harrogate. Hot-springs also occur in which but very small traces of soluble constituents are found, but which from their high temperature are used for the purpose of medicinal bathing; such springs are those of Pfäfers 44°, Gastein 35°, Bath 47°, and Buxton 28°. The waters of Bath and Buxton contain extremely small amounts of radio-active substances derived from radium, and the Bath water contains a considerable amount of dissolved helium.

(4) *Silicious Waters* are those in which the saline contents consist chiefly of alkali silicates, such as the hot-spring waters of Iceland.

The following analysis by Bunsen of the mineral waters of Dürkheim and of Baden-Baden may serve as examples of the complexity in chemical composition of certain mineral waters:—

Analyses of 1,000 *parts of the Mineral Waters in which the Alkali Metals Cæsium and Rubidium were discovered by Bunsen.*

	Dürkheim.	Baden-Baden.
Calcium bicarbonate	0·28350	1·475
Magnesium bicarbonate	0·01460	0·712
Ferrous bicarbonate	0·00848	0·010
Manganous bicarbonate	traces	traces
Calcium sulphate	—	2·202
Calcium chloride	3·03100	0·463
Magnesium chloride	0·39870	0·126
Strontium chloride	0·00818	—
Strontium sulphate	0·01950	0·023
Barium sulphate	—	traces
Sodium chloride	12·71000	20·834
Potassium chloride	0·09660	1·518
Potassium bromide	0·02220	traces
Lithium chloride	0·03910	0·451
Rubidium chloride	0·00021	0·0013
Cæsium chloride	0·00017	traces
Alumina	0·00020	—
Silica	0·00040	1·230
Free carbonic acid	1·64300	0·456
Nitrogen	0·00460	—
Sulphuretted hydrogen	traces	—
Combined nitric acid	—	0·030
Phosphates	traces	traces
Arsenic acid	—	traces
Ammoniacal salts	traces	0·008
Oxide of copper	—	traces
Organic matter	traces	traces
Total soluble constituents	18·28028	29·6393

175 *Hard and Soft Water.*—Waters are familiarly distinguished as hard and soft according as they contain large or small quantities of calcium or magnesium salts in solution. These may exist either as carbonates held in solution by carbonic acid, or as sulphates. In both cases the water is hard, that is, it requires much soap to be used in order to make a lather, because the insoluble calcium and magnesium salts are formed of the fatty

acid of the soap, which consists of sodium or potassium salts of the acids of this series. But, in the first instance, the hardness is said to be *temporary* because it is removed either by the addition of milk of lime or by boiling the water, when the carbonic acid holding the calcium carbonate in solution is either precipitated or driven off; whereas, in the second instance, it cannot be thus removed, and is therefore termed *permanent* hardness. In order to ascertain the total amount of hardness a simple method was proposed by the late Dr. Clark. It consists in ascertaining how many measures of a standard soap solution are needed by a gallon of water to form a lather. Thus this soap test serves as a rough but convenient method of determining the amount of calcium or magnesium salts which the water contains.

The following is a description of a method employed for determining the hardness of a water. 10 grams of good Castile soap are dissolved in one litre of dilute alcohol containing about 35 per cent. of alcohol, and the strength is so proportioned that 1 c.c. of this solution will precipitate exactly 1 mgrm. of calcium carbonate when in solution. In order to standardise the soap-solution 1 gram of calc-spar (Iceland spar) is dissolved in hydrochloric acid, the solution evaporated to dryness in order to get rid of the excess of hydrochloric acid, and the residue, consisting of chloride of calcium, dissolved in one litre of distilled water. Of this solution 12 c.c. are brought into a small stoppered bottle, and are diluted up to 70 c.c. with distilled water. The soap-solution is gradually added from a burette until, when vigorously shaken, a permanent lather is formed. If the solution has been made of the right strength 13 c.c. are needed for this purpose, inasmuch as 70 c.c. of distilled water will themselves require 1 c.c. of soap-solution in order to make a permanent lather. For the purpose of determining the hardness of a water, a measured quantity of the water is taken, and the standard soap-solution run in until a permanent lather is obtained: 70 c.c. of water are usually employed for this purpose, because every c.c. of the soap-solution will then correspond to one grain of calcium carbonate in 70,000, or in a gallon of water. Frequently, however, the hardness is calculated into parts per 100,000 of water. The hardness of a water is expressed in degrees, by which is understood the number of parts of calcium carbonate or of the corresponding magnesium, or other calcium salts, which are contained in 70,000 or in 100,000 parts of the water. Thus, Thames water has a hardness of 15°·0, or contains in solution 15 grains of carbonate of calcium per gallon, whilst in the water of Bala Lake only 1·3 grains per gallon are present. The presence of magnesium salts interferes to some extent with the accuracy of the determination of hardness.

176 *The Organic Constituents of Waters.*—Spring-water not only contains inorganic, but also soluble organic constituents, and these likewise vary with the constituents of the strata through which the water passes. This organic matter may be distinguished as (*a*) that which is derived from a vegetable, and (*b*) that derived from an animal source. If the water has been collected from moorland it will contain some soluble vegetable matter; if it has come in contact with any decomposing animal substances it will have taken up soluble animal matter. These two forms of impurity are of a very different degree of importance as regards the suitability of a water thus impregnated for drinking purposes.

It is now generally admitted that a number of infectious diseases, especially cholera and typhoid fever, are frequently contracted and spread by means of drinking-water containing the bacteria of these diseases, derived from the excreta or other discharges from persons suffering from them, or from the washing of infected clothing. Hence it becomes very important to be able to detect the presence of these pathogenic or disease-producing organisms. This is, however, a matter of considerable difficulty, and hence the bacteriological examination of a water is mainly valuable as a test of the efficacy of processes of purification, since the conclusion may be safely drawn that any mode of treating the water which proves fatal to the harmless bacteria, which are generally present in considerable numbers, will also prove fatal to the dangerous organisms.[1]

Some information as to the character of a water can also be obtained by estimating the number present of certain bacteria which inhabit the intestinal tract of man and animals, and are present in enormous numbers in sewage, but are absent from, or only present in very small numbers in, unpolluted waters.

The actual determination of the number of organisms of all kinds present in a sample of water, without attempting to ascertain their specific nature, is carried out by mixing a known volume of the water with sterilised nutrient gelatine and maintaining the

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[1] Frankland, *Journ. Soc. Chem. Ind.* 1887, **6**, 319.

whole at a temperature of 20—23°, which is found to be favourable to the development of these organisms, for several days. Under these circumstances each organism produces a colony around itself, and reproduction proceeds so rapidly that in a few days a mass which is visible to the naked eye is produced. The colonies are then counted and the number of bacteria which were present in the volume thus ascertained. The result of a determination of this character is not absolute, because many organisms do not develop under the conditions observed. In 1886 the water of the Lea unfiltered contained an average of 19,781 organisms per c.c., whilst after storage and filtration the same water as supplied to the consumers contained only 253 or about 1·3 per cent. of this number. Filtration through sand, charcoal, or spongy iron has the effect of removing the whole of these bacteria, but, unless the material of the filter is frequently renewed, this high state of efficiency is not maintained, and the filter may even serve as an incubating bed, so that the water passing through is rendered worse by filtration.

Simply boiling the water for a few minutes does not entirely destroy the bacteria contained in it, but greatly diminishes their number. Thus a sample of Parisian canal water which contained 460,800 bacteria per c.c. was found after boiling for ten minutes only to contain a single living organism in every 2 c.c.[1]

The chemical examination of a water is a much more rapid process, but yields even less direct information as to the wholesomeness of the sample than the bacteriological. It aims at detecting and estimating in the water such substances as are characteristic of the probable sources of pollution.

Nitrogen for example is one of the characteristic constituents of animal matter, being present in considerable quantity in a state of combination in every part of the flesh, nerves, and tissues of the body, whilst it is contained in plants in smaller quantity and mainly in their fruit and seeds. Hence if water be impregnated with animal matter this will be indicated by the presence of nitrogen in solution, either in the form of albumin or albuminous matter, if the animal matter be contained in the water unchanged, or, if the animal matter has undergone oxidation, in the form of ammonia, or nitrous or nitric acid. The amount of the nitrogen which has been converted into ammonia

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[1] Miguel, quoted in article Water, *Thorpe's Technical Dictionary.*

can be easily determined by distilling the water with sodium carbonate, when the whole of the ammonia existing in this form is obtained in the distillate and estimated by Nessler's colorimetric test. The Nessler's solution is prepared as follows:—35 grams of potassium iodide and 13 grams of mercuric chloride (corrosive sublimate) are dissolved in about 800 c.c. of hot water, and then a saturated solution of mercuric chloride is gradually added until the precipitate formed ceases to re-dissolve; 100 grams of caustic potash are then dissolved in the liquid, and the cold solution is diluted to one litre and is allowed to deposit any undissolved matter. Half a litre of the water under examination must be distilled in a glass retort, sodium carbonate having been previously added, and care having been taken to free the apparatus from ammonia by a previous process of distillation. The distillate is collected successively in volumes of 50 c.c. and the amount of ammonia in each of these separate distillates determined. For this purpose the distillate is collected in a high cylinder of white glass, 2 c.c. of Nessler's solution are added, and the mixture well stirred. A yellow coloration is produced even when only 0·0025 milligram of ammonia is present. The actual amount of ammonia is estimated colorimetrically by making up a series of solutions of equal volume containing known amounts of a standard solution of ammonium chloride, adding 2 c.c. of the Nessler reagent, and ascertaining in which of these the same tint is produced as in the distillate which is being examined. This standard solution is prepared by dissolving 3·15 grams of ammonium chloride in one litre of water and diluting 10 c.c. of this solution to one litre, so that each c.c. corresponds to 0·01 mgrm. of ammonia.

The nitrates and nitrites present can be estimated in another portion of the water by reducing these acids to ammonia by means of the hydrogen evolved by aluminium in presence of pure caustic alkali. For other methods the treatises on water analysis must be consulted.

In order to estimate the quantity of unaltered albuminous matter which may possibly be contained in the water, two processes have been proposed. The first of these, proposed by Wanklyn and Chapman, depends upon the fact that these albuminous bodies are either wholly or in part decomposed on distillation with an alkaline solution of potassium permanganate, the nitrogen being in this case again evolved as ammonia which is determined as above. In the second process, described by Frankland and Armstrong, the nitrogen contained combined in albuminous matter in the water is liberated in the gaseous state by a combustion analysis performed on the dry residue of the water, the volume of the free nitrogen being afterwards carefully measured. In this latter process not only the *organic nitrogen* but also the *organic carbon*, that is, the carbon derived from animal and vegetable sources, can be quantitatively determined.

A further test which is often applied is the estimation of the amount of potassium permanganate which is reduced by the substances contained in the water. Many modifications of this test are employed, acid solutions being used in some processes, and alkaline solutions in others, whilst the temperature and the duration of the experiment are also varied. In any case the results are only valuable for comparative tests, and do not, like those of the Frankland combustion process, give an absolute value for the organic matter.

Finally, the organic nitrogen may be determined by a modification of Kjeldahl's method, according to which the dry residue is heated with sulphuric acid, whereby the whole of the organic nitrogen is converted into ammonia, which is then estimated as usual.

If a water is found to contain more than 0·01 part of albuminoid nitrogen in 100,000 parts of water, it may, as a rule, be considered as unfit for drinking purposes; many surface well-waters occur in large towns in which the amount of albuminoid nitrogen reaches 0·03 to 0·08 part per 100,000, and such waters must be regarded as little better than sewage, and, therefore, as absolutely poisonous. But water in which no albuminous matter has been found may also have been largely impregnated with sewage or infiltrated animal impurity, the greater part of which has undergone oxidation. Thus when the amount of free ammonia exceeds 0·01 part per 100,000, it almost invariably proceeds from the decomposition of urea into ammonium carbonate, and shows that the water consists of diluted urine. In like manner, when the oxidation has proceeded further, the nitrogen will be found as nitrates and nitrites, and should any considerable quantity of these substances be found in surface, well, or river water, the previous admixture of animal impurity may be inferred.

177 The water analyst is also assisted in his attempts to indicate the limits of wholesomeness in a water by the determination of the amount of chlorine present as chloride of sodium, &c., which the water contains. Not that chlorides are in themselves of importance, but because their presence serves as an indication of sewage contamination, for pure natural waters are almost free from chloride of sodium, whilst urine and sewage are highly charged with this substance. So that, if we meet with a water almost free from chlorine, it cannot have come into contact with sewage. Thus the water of Ullswater contains from 0·7 to 0·8 grain of chlorine in the gallon (1—1·1 parts per 100,000), whilst many surface wells in large towns may be found which contain from 10 to above 30 grains of chlorine per gallon (14—43 parts per 100,000). Taken alone, the chlorine test cannot be relied upon, as many pure well-waters occur, such as those in Cheshire, in the neighbourhood of the salt beds, or near the sea, which contain common salt. If, however, this test be employed in conjunction with those previously mentioned, the evidence for or against a water is rendered much more cogent. As a rule it may be said that waters containing more than two grains of chlorine per gallon (2·85 parts per 100,000) must be looked upon with suspicion, unless indeed some good reason for the presence of common salt can be assigned.[1]

It will be noted that the object which the water analyst has in view is to determine whether or not a water is liable to contamination by the drainage from animal, and especially human, excreta, it being held that all water so contaminated is dangerous, not because of the actual presence of the constituents of the sewage, but because sewage is the channel by which pathogenic organisms may at any time find access to the water.

The following analyses serve to show the difference between a good potable water and one which is totally unfit for drinking purposes. No. 1, the water supplied by the Manchester Corporation from the Derbyshire hills; No. 2 is a surface-well

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[1] For the special details of the processes of water analysis, the following works or memoirs may be consulted:—*Water Analysis*, by Wanklyn and Chapman. 1889. Trübner, London. Frankland and Armstrong, *Journ. Chem. Soc.* 1868. p. 77; Frankland, *ibid.*, 109; also *Journ. Chem. Soc.*, June, 1876. Percy Frankland, *Agricultural Chemical Analysis*, p. 257. Macmillan, 1883. *Volumetric Analysis*, by Sutton (1900), 446 (Churchill). The general question of water supply is treated by Thresh: *Water Supplies.* (The Rebman Publishing Co.)

water, at one time used for drinking purposes in a manufacturing town, although little better than effluent sewage.

—	No. 1. Good Water.		No. 2. Bad Water.	
	Parts per 100,000.	Grains per Gallon.	Parts per 100,000.	Grains per Gallon.
Total solids	6·30	4·4	53·0	37·1
Nitrogen as nitrites and nitrates	0·025	0·017	0·78	0·546
Free ammonia . . .	0·003	0·002	0·432	0·303
Albuminoid ammonia .	0·007	0·005	0·09	0·063
Chlorine	1·14	0·8	6·9	4·8
Temporary hardness .	—	0·1	—	7·2
Permanent hardness .	—	2·4	—	14·4
Total hardness . . .	—	2·5	—	21·6

178 *River-Waters.*—The composition of river-water varies considerably with the nature of the ground over which the water runs: thus, Thames water contains about 11 grains per gallon of calcium carbonate; the Trent, 21 grains of calcium sulphate; or they are both hard waters, the first temporarily and the second permanently hard. The waters of the Dee and the Don, in Aberdeenshire, draining a granite district, are, on the other hand, soft waters. The composition of these waters is shown in the table on the next page.

Unfortunately in England, as in other manufacturing and densely populated countries, the running water seldom reaches the sea in its natural or pure state, but is largely contaminated with the sewage of towns, or the refuse from manufactures or mines. So serious indeed is this state of things that steps have been taken to prevent the further pollution of the rivers of the country, and Royal Commissions have reported and several Acts of Parliament have been passed with a view of preventing the evil. The following analyses of the composition of Lancashire rivers, taken from the First Report of the Commissioners[1] appointed in 1868, show clearly the pollution which the originally pure waters of the Irwell and Mersey undergo on flowing down to the sea.

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[1] P. 15.

TABLE GIVING THE COMPOSITION OF CERTAIN RIVER-WATERS.

—	Grains per gallon.			
	Thames.	Trent.	Dee.	Don.
Calcium carbonate . . .	10·80	0·32	0·85	2·23
Calcium sulphate	3·00	21·55	0·12	0·13
Calcium nitrate	0·17	—	—	—
Magnesium carbonate . .	1·25	5·66	0·36	1·07
Sodium chloride	1·80	17·63	0·72	1·26
Silica	0·56	0·72	0·14	0·52
Ferric chloride and alumina	0·27	0·50	0·06	0·27
Calcium phosphate . . .	trace	trace	trace	trace
Organic matter	2·36	3·68	1·54	3·06
	20·21	50·06	3·79	8·54
Hardness	14·0	26·5	1·5	3·0

COMPOSITION OF LANCASHIRE RIVERS.

Parts in 100,000.

—	IRWELL.		MERSEY.	
	*1	2	3	4
Total soluble solids . . .	7·8	55·80	7·62	39·50
Organic carbon	0·187	1·173	0·222	1·231
Organic nitrogen	0·025	0·332	0	0·601
Ammonia	0·004	0·740	0·002	0·622
Nitrogen as nitrates and nitrites	0·021	0·707	0·021	0
Total combined nitrogen .	0·049	1·648	0·023	1·113
Chlorine	1·15	9·63	0·94	—
Total hardness	3·72	15·04	4·61	10·18
SUSPENDED MATTER—				
Organic	0	2·71	0	—
Mineral	0	2·71	0	—
Total	0	5·42	0	—

*1. The Irwell near its source.
2. The Irwell at Manchester.
3. The Mersey, one of its sources.
4. The Mersey below Stockport.

From these numbers it is seen that the quantities of free ammonia and nitric acid became increased 300- or 400-fold in the river at Manchester, whilst the total combined nitrogen was increased from 0·049 to 1·648.

179 *Sea-Water.*—The amount of solid matter contained in the waters of the ocean is remarkably constant when collected far from land. The mean quantity is about 35·976 grams in 1,000 grams of sea-water; the average specific gravity of sea-water is 1·02975 at 0°.

COMPOSITION OF THE WATER OF THE IRISH SEA IN THE SUMMER OF 1870.[1]

One thousand grams of sea-water contain	Grams.
Sodium chloride	26·43918
Potassium chloride	0·74619
Magnesium chloride	3·15083
Magnesium bromide	0·07052
Magnesium sulphate	2·06608
Magnesium carbonate	traces
Magnesium nitrate	0·00207
Calcium sulphate	1·33158
Calcium carbonate	0·04754
Lithium chloride	traces
Ammonium chloride	0·00044
Ferrous carbonate	0·00503
Silicic acid	traces
	33·85946

For the purpose of controlling the analysis, 1,000 grams of water were evaporated to dryness, and the dry residue weighed. Its weight was found to be 33·83855 grams. The specific gravity of the water at 0° C. was 1·02721, whilst that at 15° C. was 1·02484.

Forchhammer found that 1,000 parts by weight of the water of the mid-Atlantic Ocean contained 35·976 parts of dissolved salts, whilst the mean of analyses of sea-water from different localities gave 34·082 for the total salts in summer and 33·838

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[1] Thorpe and Morton, *Journ. Chem. Soc.* 1871, **24**, 506.

in winter. Dittmar,[1] on the other hand, from 77 specimens of sea-water collected on board the *Challenger* in various parts of the world, concludes that the maximum quantity of salt contained in the water of the Indian Ocean is 33·01, and in that of the North Atlantic 37·37. In the neighbourhood of the shore or in narrow straits the quantity of saline matter is often much smaller.

According to Forchhammer the relation in which the several salts stand to one another is a constant one; and in this conclusion Dittmar agrees. The former calculated the quantity of lime, magnesia, potash, and sulphuric acid present with 100 parts of chlorine, including bromine. Dittmar estimated this element and also soda and carbon dioxide, and then calculated as Forchhammer, reckoning the bromine as its equivalent of chlorine. Their results are:—

	Forchhammer.	Dittmar.		Forchhammer.	Dittmar.
Cl	100·00	99·848	CaO	2·93	3·026
Br	—	0·3	MgO	11·03	11·221
SO_3	11·88	11·576	K_2O	1·93	2·405
CO_2	—	0·276	Na_2O	—	74·462

Dittmar calculated the following average composition of the total saline constituents of sea-water, giving a somewhat different arrangement to the acids and bases from that adopted by Thorpe and Morton.

Sodium chloride	77·758	Magnesium bromide	0·217
Magnesium chloride	10·878	Calcium carbonate	0·345
Magnesium sulphate	4·737		
Calcium sulphate	3·600		100·000
Potassium sulphate	2·465		

All the elements are doubtless contained in sea-water. In addition to those named above the following have been detected:—

Iodine, fluorine, nitrogen, phosphorus, silicon, carbon, boron, zinc, cobalt, nickel, copper, strontium, barium, manganese, aluminium, iron, lithium, cæsium, rubidium (these three detected spectroscopically), silver, lead, gold, and lastly arsenic, making a total of over thirty elements.

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[1] *Challenger Reports*, "On the Composition of Ocean Water." By Professor Dittmar, F.R.S. London, 1884.

HYDROGEN DIOXIDE, HYDROGEN PEROXIDE, OR HYDROPEROXIDE. $H_2O_2 = 33{\cdot}76$.

180 This body was discovered in 1818 by Thénard,[1] who prepared it, by the action of dilute hydrochloric acid on barium dioxide, thus:—

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$

This compound is also easily obtained by passing a current of carbon dioxide through water, and gradually adding barium dioxide in very small quantities,[2] thus:—

$$BaO_2 + CO_2 + H_2O = H_2O_2 + BaCO_3.$$

It is also produced in many cases during oxidation; thus Traube[3] has shown that it is formed by the action of oxygen on zinc, cadmium, and palladium-hydrogen (see page 248), whilst Gorup *v.* Besanez[4] found that an oxidising substance, probably consisting of the dioxide, is formed during the evaporation of water. Further, when a jet of burning hydrogen,[5] carbonic oxide, or of the vapours of ether and alcohol[6] is allowed to impinge on water, the latter shows the reactions of hydrogen dioxide. According to Richardson[7] it is also produced by the action of direct sunlight on urine, and in presence of oxygen on ether, amyl alcohol, and certain organic acids.

Preparation.—Hydrogen dioxide is, however, most generally obtained by decomposing pure barium dioxide with dilute sulphuric acid; thus:—

$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4.$$

The pure barium dioxide needed for these experiments is prepared as follows:—commercial barium dioxide, very finely powdered, is brought little by little into dilute hydrochloric acid, until the acid is nearly neutralised. The cooled and filtered solution is then treated with baryta-water, in order to precipitate the ferric oxide, manganese oxide, alumina, and silica which are

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[1] *Ann. Chim. Phys.* 1818, **8**, 306.

[2] Duprey, *Compt. rend.* 1862, **55**, 736; Balard, *Compt. rend.* 1862, **55**, 758.

[3] *Ber.* 1893, **26**, 1471.

[4] *Annalen*, 1859, **111**, 232.

[5] Bach, *Compt. rend.* 1897, **124**, 951.

[6] Engler, *Ber.* 1900, **33**, 1109.

[7] *Journ. Chem. Soc.* 1893, 1110; 1896, 1349.

always present. As soon as a white precipitate of the hydrated barium dioxide makes its appearance, the solution is filtered, and to the filtrate concentrated baryta-water is added; a crystalline precipitate then falls consisting of hydrated barium dioxide. This is well washed and preserved, in the moist state, in stoppered bottles. In order to prepare hydrogen dioxide by means of this substance, the moist precipitate is gradually added to a cold mixture of not less than five parts of water to one part of concentrated sulphuric acid, until the mixture remains very slightly acid. The precipitate of barium sulphate is allowed to settle, and the liquid filtered. The small trace of sulphuric acid which the filtrate contains can be precipitated by careful addition of dilute baryta solution.

The dilute aqueous solution thus obtained may be concentrated by allowing it to stand over sulphuric acid *in vacuo*, by careful heating in open dishes, or by fractionating in vacuo, when the water volatilises more rapidly than the dioxide. The last portions of the water may be removed by repeated applications of the last named method, or the concentrated solution may be extracted with ether, which readily dissolves the dioxide, and the resulting solution then fractionated.[1] If, however, ether be used, great care must be taken in the distillation, as an organic peroxide, or higher oxide of hydrogen, appears to be sometimes formed which may explode with great violence.

For many purposes it is not necessary that the hydrogen dioxide solution should be free from alkali-salts, and in such cases the solution may readily be prepared by the action of cold dilute acids on potassium percarbonate or sodium peroxide, both of which compounds are now manufactured on the large scale.

The pure dioxide may also be prepared by distillation from the latter solution, if sulphuric acid be used in neutralising the sodium dioxide.[2]

181 *Properties.*—Pure dry hydrogen dioxide is a syrupy liquid having a strongly acid reaction, which is colourless in small quantity, but when viewed in bulk, has, like water, a bluish colour. It has a specific gravity of 1·4584 at 0° (Brühl), and boils at 69·2° under 26 mm., and at 84–85° under 68 mm. pressure, and has recently been obtained[3] in the form of anhydrous prisms, melting at $-2°$.

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[1] Spring, *Zeit. anorg. Chem.* 1895, **8**, 424; Wolffenstein, *Ber.* 1894, **27**, 3307; Brühl, *Ber.* 1895, **28**, 2847.

[2] Merck, *Chem. Centr.* 1904, ii. 67.

[3] Staedel, *Zeit. angew. Chem.* 1902, **15**, 642.

The pure distilled compound, containing 95–100 per cent. of H_2O_2, is a fairly stable substance, being scarcely changed after standing for seven weeks, provided that direct sunlight be excluded, and that the bottle containing it has a smooth surface. Roughness of surface, the presence of finely divided solid matter, or prolonged shaking, greatly accelerates the rate of decomposition. In aqueous solution decomposition only takes place slowly, if this does not contain free alkali, salts of heavy metals, or suspended solid matter; but in presence of these, a moderately concentrated solution loses oxygen slowly at the ordinary temperature, with simultaneous formation of water, and at 100° the evolution of gas becomes so rapid that explosions may ensue.

Thénard found that 1 volume of the pure liquid yielded 475 times its volume of oxygen at 14° and 760 mm., the amount theoretically required by the formula H_2O_2 being 501·8 volumes; the deficiency of oxygen found is due to the fact that, on heating, small quantities of the dioxide are volatilised unchanged together with the steam which is also evolved. The molecular weight determined by the lowering of the freezing point in aqueous solutions also agrees with this formula.[1]

Although finely divided solid matter of any kind appears to facilitate materially the decomposition of hydrogen dioxide into oxygen and water, some substances have a much more pronounced action than others. Finely divided metals, such as gold, silver, and platinum, cause the decomposition of the anhydrous compound with almost explosive violence, although the metals themselves finally remain unaltered. It has been shown by Bredig[2] that a very small quantity of the colloidal solution of such metals is able to effect the decomposition of large quantities of the dioxide, the action resembling that of a ferment, hence such solutions have been termed "inorganic ferments." The colloidal metallic solutions are obtained by passing an electric discharge between poles of the metal immersed in water, and their power of decomposing hydrogen dioxide is, as in the case of the specific action of some of the ferments, paralysed for a time by the addition of "poisons" such as hydrocyanic acid, sulphuretted hydrogen, or mercuric chloride.

From the experiments of Liebermann[3] it seems probable that

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[1] Carrara, *Gazzetta*, 1892, **22**, ii. 141; Tammann, *Zeit. physikal. Chem.* 1893, **12**, 431.

[2] *Zeit. physikal. Chem.* 1899, **31**, 258; 1901, **37**, 1, 323; 1901, **38**, 122.

[3] *Ber.* 1904, **37**, 1519.

this action of finely divided metals is an indirect one, the latter acting first on the oxygen of the air and "rendering it active" (p. 247); the decomposition is then brought about by the combination of the "active" oxygen with the additional oxygen atom of the hydrogen dioxide, with formation of ordinary diatomic oxygen molecules, the action being therefore analogous to that of the dioxide on certain metallic oxides next to be considered.

The oxides of metals such as gold, silver, and platinum immediately cause the decomposition of the dioxide into water and oxygen even in dilute aqueous solution, and the oxides themselves are simultaneously reduced to the metallic state, the reaction with silver oxide being represented by the equation:[1]—

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

We have here the remarkable phenomenon of a powerful oxidising agent exerting a reducing action on metallic oxides with formation of the metal. The explanation of this fact is, however, not far to seek. The above-named metals only combine somewhat feebly with oxygen, and their oxides easily decompose into the elements. When they are brought into contact with hydrogen dioxide, which contains one atom of oxygen but feebly united, mutual reduction takes place, the one atom of oxygen in the dioxide combining with one atom of oxygen in the metallic oxide to form a molecule of free oxygen.

Some doubt has been thrown by Berthelot[2] on the equation given above, but the renewed investigation of the reaction by Baeyer and Villiger[3] has confirmed the results of Thénard.

The decomposition of hydrogen dioxide is also affected by a class of organic ferments termed the *catalases*, which occurs most widely distributed throughout the animal and vegetable kingdoms.[4] It is also slowly decomposed by ozone.[5]

182 When baryta-water (barium hydroxide) is mixed with hydrogen dioxide, a precipitate of barium peroxide separates out:—

$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O.$$

If an excess of hydrogen dioxide be left in contact with the

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[1] Thénard, *Ann. Chim. Phys.* 1819, **9**, 96.

[2] *Ann. Chim. Phys.* 1897 [7], **11**, 217; 1902 [7], **25**, 78.

[3] *Ber.* 1902, **34**, 749, 2769.

[4] Loew, *U.S. Dept. of Agriculture Report*, 1900.

[5] Inglis, *Journ. Chem. Soc.* 1903, 1013.

barium peroxide, oxygen is slowly evolved until the whole of the former is decomposed, the barium peroxide remaining unaltered. According to Schöne and de Forcrand, the white compound BaO_2,H_2O_2 is first formed, and then slowly decomposes into barium peroxide, water, and free oxygen.

Many other basic oxides are converted by hydrogen dioxide into peroxides, especially in presence of alkali. Thus manganous salts are in this way converted into manganese dioxide, whereas these peroxides in presence of an acid are again reduced by hydrogen dioxide to basic oxide. Thus if hydrogen dioxide be brought into contact with dilute sulphuric acid and manganese dioxide, oxygen is given off and manganous sulphate formed:—

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2.$$

The decomposition here occurring is similar to that which takes place in the reduction of silver oxide, the change being assisted by the presence of acid, which reacts with the basic oxide to form a soluble salt.

Towards certain salts hydrogen dioxide acts as an acid: thus on addition of a solution of potassium or sodium carbonate it is completely converted into the peroxide of the metal, with evolution of carbon dioxide. If, however, the dioxide be added gradually to the solutions of the carbonates, pure oxygen is evolved.[1]

Hydrogen dioxide also forms molecular compounds with certain salts, in which it appears to play the same part as water of crystallisation,[2] such as

$$(NH_4)CrO_5,H_2O_2;\ KCrO_5,H_2O_2;\ (NH_4)_2SO_4,H_2O_2.$$

Hydrogen dioxide acts as a strong bleaching agent for organic colouring matters, these being completely destroyed by oxidation, as with chlorine, but the action is less rapid than with the latter. It is now largely employed for bleaching straw, silk, and wool, being manufactured for this purpose by dissolving sodium peroxide (Vol. II. (1897), p. 163) in water, and adding dilute sulphuric acid; the product is sold under the name of *soda-bleach*. It is also used for bleaching and cleaning old stained engravings and oil-paintings, and as an auricome for bleaching dark-coloured hair.

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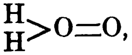
[1] Spring, *Zeit. anorg. Chem.* 1895, **10**, 161.

[2] Weide, *Ber.* 1898, **31**, 516; Willstätter, *Ber.* 1903, **36**, 1828.

Hydrogen Dioxide in the Atmosphere.—The same doubt exists as to the presence of hydrogen dioxide in the air as is the case with ozone (p. 265). Schöne[1] maintains that it is present in the air, rain, and snow, but Ilosva[2] states that the evidence for its presence is inconclusive, as oxides of nitrogen are always present in these, and may cause the oxidising effects observed by Schöne.

183 *Constitution of Hydrogen Dioxide.*—The exact constitution of the dioxide has not yet been ascertained with certainty. It is usually represented by the structural formula H.O.O.H, in which both atoms of oxygen are divalent. In view, however, of the readiness with which one atom of oxygen is evolved, the constitution  $\begin{matrix}H\\H\end{matrix}\!>O{=}O$, in which one atom of oxygen is tetravalent and one divalent, has been suggested by Kingsett,[3] whilst Brühl[4] proposes the formula $H.O{\equiv}O.H$, in which both oxygen atoms are tetravalent, this formula being in better agreement with certain physical constants of the compound than the first.

184 *Detection and Estimation of Hydrogen Dioxide.*—In order to detect the presence of hydrogen dioxide in solution, the liquid is rendered acid with sulphuric acid, some ether and a few drops of potassium chromate are added, and the solution well shaken. If hydrogen dioxide be present, the solution assumes a beautiful blue colour, and on allowing it to stand the colour is taken up by the ether, and a deep blue layer separates out. This blue compound is probably perchromic acid, and the reaction may, in a similar way, be employed for the detection of chromium.[5] Solutions of titanic and vanadic acids are turned red or brown by the dioxide, and with a mixture of potassium chlorate and aniline in presence of acid it gives a violet coloration after three minutes,[6] whilst if dimethylaniline be substituted for aniline, one part of the dioxide in five millions gives a perceptible yellow coloration.[7] A still more delicate test is its action on a solution of potassium iodide and ferrous sulphate, when iodine is liberated and detected by the formation of the blue iodide of starch (Schönbein). One part of the

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[1] *Ber.* 1874, **7**, 1695; 1893, **26**, 3011; 1894, **27**, 1233; *Zeit. anal. Chem.* 1894, **33**, 137.

[2] *Ber.* 1894, **27**, 920.

[3] *Chem. News*, 1884, **46**, 141.

[4] *Ber.* 1895, **28**, 2837.

[5] Moissan, *Compt. rend.* 1883, **97**, 96; Berthelot, *Compt. rend.* 1889, **108**, 24.

[6] Bach, *Compt. rend.* 1894, **119**, 1218.

[7] Ilosva, *Ber.* 1895, **28**, 2029.

dioxide in twenty-five million parts may thus be detected. Other oxidising agents have the power of liberating iodine from iodide of potassium, but not in presence of ferrous sulphate.

For the purpose of determining the quantity of hydrogen dioxide present in a solution, the liquid is acidified with sulphuric acid, and then a standard solution of potassium permanganate added, until the purple tint no longer disappears. The reaction here occurring is thus represented:—

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

For the quantitative determination of small quantities, Schöne[1] employed a colorimetric method, based on the fact that a neutral solution of hydrogen dioxide gradually liberates iodine from a similar solution of potassium iodide, thus:—

$$H_2O_2 + 2KI = 2KOH + I_2;$$

the depth of colour produced in presence of starch is compared with that obtained by adding known quantities of the dioxide to a solution of potassium iodide and starch. The results are, however, only reliable in the complete absence of the numerous other substances which also liberate iodine.

Higher Oxides of Hydrogen.—Oxides of hydrogen having the formulæ H_2O_3 and H_2O_4 have been described[2]; but the evidence as to their existence is as yet inconclusive.[3] According to Baeyer and Villiger,[4] potassium and rubidium peroxides, K_2O_4 and Rb_2O_4, are salts of the compound H_2O_4, which they term *ozonic acid*; but the latter has not yet been isolated.

OXYGEN AND CHLORINE.

OXIDES AND OXY-ACIDS OF CHLORINE.

185 Although chlorine and oxygen do not combine directly, three distinct compounds of these elements may be obtained by indirect means. A fourth oxide, described by Millon and others as chlorine trioxide, has been proved to be a mixture of free chlorine

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[1] *Ber.* 1874, **7**, 1695; *Annalen*, 1879, **195**, 228.

[2] Berthelot, *Compt. rend.*, 1900, **131**, 637; Bach, *Ber.*, 1900, **33**, 1506.

[3] Armstrong, *Proc. Chem. Soc.*, 1900, **16**, 134; Ramsay, *Journ. Chem. Soc.*, 1901, 1324.

[4] *Ber.* 1902, **35**.

and chlorine peroxide.[1] We are acquainted with no less than four compounds of chlorine with oxygen and hydrogen, which are known as the oxy-acids of chlorine. The following are the compounds of chlorine, oxygen, and hydrogen as yet known:—

Oxides.	Oxy-acids.
Chlorine monoxide, Cl_2O	Hypochlorous acid, $HClO$
	Chlorous acid, . . $HClO_2$
Chlorine peroxide, ClO_2	
	Chloric acid, . . $HClO_3$
Chlorine heptoxide, Cl_2O_7	Perchloric acid, . . $HClO_4$

Chlorine and oxygen can only be made to combine together in the presence of a basic oxide; thus, if chlorine gas be led over dry mercuric oxide, chlorine monoxide and mercuric oxychloride are formed; thus:—

$$2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O.$$

The same reaction takes place in presence of water, and in this case a colourless solution of the corresponding hypochlorous acid is formed:

$$Cl_2O + H_2O = 2ClOH.$$

When chlorine is passed into a cold dilute solution of an alkali such as caustic potash, instead of the free hypochlorous acid the corresponding salt, termed a hypochlorite, is formed; thus:—

$$2KOH + Cl_2 = KOCl + KCl + H_2O.$$

If the solution of the alkali be concentrated, or hot, and an excess of the gas passed through it, a salt called a chlorate is produced, the hypochlorite first formed being under these conditions converted into chlorate and chloride; thus:—

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

From the potassium chlorate thus prepared, chloric acid itself can be obtained, and by reduction of this acid the oxide ClO_2 may be prepared. Perchloric acid is prepared by the further oxidation of chloric acid, whilst dehydration of perchloric acid at a low temperature gives rise to the oxide Cl_2O_7. The oxides corresponding to chlorous and chloric acids, viz., Cl_2O_3 and

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[1] Garzarolli-Thurnlackh, *Annalen*, 1881, **209**, 184.

Cl_2O_5, have not yet been prepared. The oxides and oxy-acids of chlorine are unstable compounds, as indeed might be expected, owing to the feeble combining power which chlorine and oxygen exhibit towards one another; in consequence of this they act as powerful oxidising substances, many of them being most dangerously explosive bodies, which suddenly decompose into their constituents on rise of temperature, or even on percussion. It is, however, remarkable that perchloric acid, which contains the most oxygen, is the one which is the most stable.

CHLORINE MONOXIDE OR HYPOCHLOROUS ANHYDRIDE. Cl_2O.

186 So long ago as 1785 Berthollet noticed that chlorine could be combined with an alkali and yet preserve the peculiar bleaching power which had been previously discovered by Scheele, and it is to Berthollet that we owe the practical application of this important property. In his first experiments on this substance he employed chlorine water, but afterwards he absorbed the gas by a solution of caustic potash; and the liquor thus obtained, called Eau de Javelles from the name of a bleach-works where it was prepared, was employed for bleaching purposes on the large scale. Berthollet described these experiments to James Watt, who was at that time staying in Paris, and he brought the news to Glasgow, where Tennant, in 1798, patented an improved process for bleaching, in which lime was employed instead of the potash, as being a much cheaper substance.[1]

Up to the year 1810, when Davy proved the elementary nature of chlorine, the bleaching liquors were supposed to contain oxygenated muriates of the base. Indeed their constitution remained doubtful until the year 1834, when Balard[2] showed that the alkaline bleaching compounds may be considered to be a mixture or combination of a chloride and a hypochlorite. Eau de Javelles therefore contains potassium chloride and hypochlorite, and bleaching-powder solution the corresponding calcium salts; solid bleaching-powder has, however, a different constitution (Vol. II., 1897, p. 427).

Preparation.—Chlorine monoxide is obtained, as seen in

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[1] Tennant's first patent was declared invalid three years after it had been granted, as it was proved that bleachers in Lancashire and at Nottingham had employed lime instead of potash before the year 1798.

[2] *Ann. Chim. Phys.* 1834, **57**, 225.

Fig. 92, by the action of dry chlorine gas upon cold dry oxide of mercury, which is contained in a tube (a b), cooled by means of ice or a stream of cold water.[1] The crystallised mercuric oxide can, however, not be used for this purpose, as it is not acted on by dry chlorine, and hence the precipitated oxide must be employed, it having been previously carefully washed and dried at 300–400°. The reaction which takes place in this case has already been described (p. 338). Mercuric chloride, $HgCl_2$, is not formed in this reaction, but the oxychloride, $HgO, HgCl_2$.

187 *Properties.*—Chlorine monoxide is a brownish-yellow coloured gas, which has a peculiar penetrating smell, somewhat resembling, though distinct from, that of chlorine. Its density is 43·5.[2] By exposure to a low temperature the gas can be condensed, as in the tube (D), Fig. 92, to an orange-coloured liquid, which boils at about + 5°. If an attempt be made to seal up this liquid in the tube in which it has been prepared, or even if the tube in which it is contained be scratched with a file, it decomposes suddenly with a most violent explosion (Roscoe); and when poured out from one vessel to another a similar explosion takes place (Balard). It likewise explodes on heating, but not

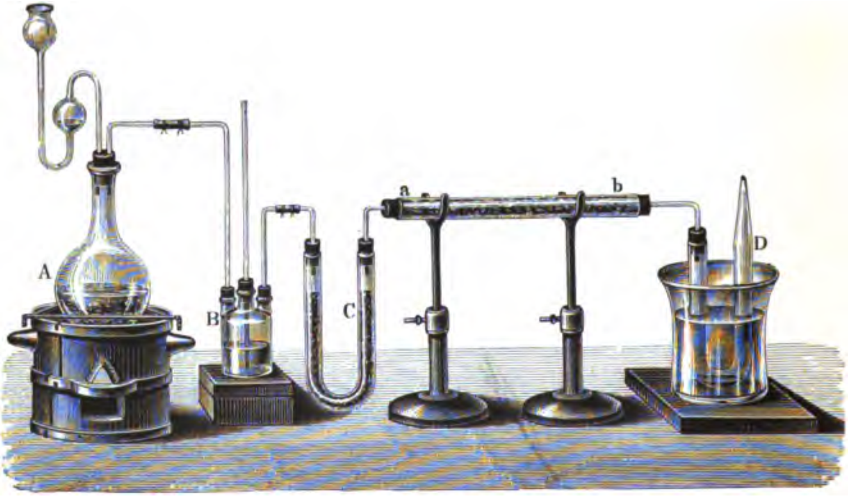

FIG. 92.

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[1] V. Meyer, *Ber.* 1883, **16**, 2999; Ladenburg, *Ber.* 1884, **17**, 157.

[2] Thurnlackh and Schacherl, *Annalen*, 1885, **230**, 273.

so violently, two volumes decomposing into one volume of oxygen and two of chlorine. According to Garzarolli-Thurnlackh and Schacherl it does not, contrary to previous statements, undergo decomposition in direct sunlight, and the liquid, if all organic matter be carefully excluded, may be distilled without decomposition. Most easily oxidisable substances and many finely divided metals take fire in the gas and produce an explosion; the gas is also decomposed in presence of hydrochloric acid into free chlorine and water.

$$2HCl + Cl_2O = 2Cl_2 + H_2O.$$

Chlorine monoxide is readily soluble in water, the latter dissolving 200 vols. or 0·78 of its weight of the gas at 0°. The solution has an orange-yellow colour.

HYPOCHLOROUS ACID. $HClO$.

188 The aqueous solution of chlorine monoxide must be considered as a solution of hypochlorous acid, a compound which in the pure state is unknown.

Preparation.—(1) The solution is best prepared by shaking chlorine-water with precipitated mercuric oxide,[1] when the oxide quickly dissolves and the colour of the solution disappears, thus:—

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2ClOH.$$

The liquid is now distilled in order to remove the mercuric chloride, the distillate consisting of aqueous hypochlorous acid.

(2) An aqueous solution of hypochlorous acid is also easily obtained by adding to a solution of bleaching-powder exactly the amount of a dilute mineral acid requisite to liberate the hypochlorous acid (Gay-Lussac). For this purpose a dilute nitric acid containing about 5 per cent. of the pure acid is allowed to run slowly from a burette into a filtered solution of common bleaching-powder, whilst the liquid is kept well stirred in order to prevent a local super-saturation which would cause a liberation of the hydrochloric acid of the chloride, and thus again effect a decomposition of the hypochlorous acid into chlorine and water. If this operation be conducted with care, no chlorine is evolved, or at any rate only a trace if a slight

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[1] Gay-Lussac, *Annalen*, 1842, **43**, 158.

excess of nitric acid has been added, and the distillate is perfectly colourless. Boric acid may also be employed with advantage for liberating hypochlorous acid from its salts.[1]

(3) Another method of obtaining the aqueous acid is to saturate a solution of bleaching-powder with chlorine, then to drive off the excess of chlorine by passing a current of air through the liquid, and then to distil. The following equation represents the reaction which here occurs:—

$$Ca(OCl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4ClOH.$$

In place of bleaching-powder baryta-water may be employed, when barium hypochlorite is at first formed, and afterwards decomposed as shown above.[2]

(4) Hypochlorous acid is so weak an acid that its salts are decomposed by carbonic acid, so that if chlorine gas be led into a cold solution of a carbonate, or passed through water containing finely divided calcium carbonate in suspension (1 part to 40 of water), no hypochlorite is formed, but only hypochlorous acid (Williamson); thus:—

$$CaCO_3 + 2Cl_2 + H_2O = 2ClOH + CaCl_2 + CO_2.$$

Other salts of the alkali-metals act in a similar way when a stream of chlorine is passed through their cold aqueous solutions; this is the case with sulphate and phosphate of sodium, an acid salt being formed in these cases;

$$Na_2SO_4 + H_2O + Cl_2 = NaCl + NaHSO_4 + ClOH;$$

whilst if sodium chloride be warmed with hypochlorous acid, sodium chlorate and free chlorine are produced (Williamson).

Concentrated aqueous solutions of hypochlorous acid have an orange yellow or golden yellow colour, and an odour somewhat resembling that of chloride of lime. Only dilute solutions of hypochlorous acid can be distilled without decomposition; concentrated solutions are readily decomposed either on heating or on exposure to sunlight, part splitting up into chlorine and oxygen, whilst another part undergoes oxidation, yielding chloric acid. It is slowly decomposed by platinum black, forming hydrochloric and chloric acids.[3]

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[1] Lauch, *Ber.* 1885, **18**, 2287.

[2] Williamson, *Chem. Soc. Mem.* 1850, **2**, 234.

[3] Foerster and Müller, *Zeit. Electrochem.* 1902, **8**, 515.

Aqueous hypochlorous acid dissolves iron and aluminium with production of hydrogen and chlorine; with copper, nickel, and cobalt, chlorine and oxygen are evolved, whilst magnesium yields pure hydrogen.[1]

Hypochlorous acid has a bleaching power twice as great as that of chlorine water containing the same amount of chlorine.[2] The explanation of this fact is evident from a consideration of the following equations, which also indicate that the bleaching effect produced by chlorine is in reality due to a decomposition of water, the chlorine combining with the hydrogen and liberating the oxygen. It is, therefore, this latter element which is the true bleaching agent, inasmuch as it oxidises and destroys the colouring agent.

(*a*) Bleaching action of chlorine water;

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

(*b*) Bleaching action of the hypochlorous acid formed from the chlorine water;

$$2ClOH = 2HCl + O_2.$$

Hydrogen dioxide converts hypochlorous acid into hydrochloric acid and free oxygen, whilst the hypochlorites with the same reagent yield the corresponding chloride. When hypochlorous acid and a hypochlorite are both present, the amount of free acid may therefore be determined by adding hydrogen dioxide, and estimating the amount of hydrochloric acid produced.[3]

The hypochlorites, like the acid, are unstable compounds, which in the pure state are almost unknown. Of these the most important, calcium hypochlorite, $Ca(OCl)_2$, is formed when bleaching-powder is dissolved in water although it is probably not present as such in the solid substance, and it is to the presence of this compound that the bleaching properties of the solution are due, inasmuch as when either hydrochloric or sulphuric acid is added, a quantity of chlorine equal to that contained in the compound is evolved. In the first case, one half of the chlorine is derived from the hypochlorite, and the other half from the hydrochloric acid, which first liberates hypochlorous acid, and then decomposes it into chlorine and water; thus:—

$$(1)\quad 2HCl + Ca(OCl)_2 = 2HOCl + CaCl_2.$$

$$(2)\quad 2HCl + 2HOCl = 2H_2O + 2Cl_2.$$

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[1] White, *J. Soc. Chem. Ind.* 1903, **22**, 132.

[2] Gay-Lussac, *Annalen*, 1842, **43**, 161.

[3] Siewerts, *Zeit. Electrochem.* 1900, **6**, 364.

If sulphuric acid be used, the result is the same, as this acid decomposes the calcium chloride; thus:—

$$CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 2Cl_2.$$

Solutions of all hypochlorites slowly undergo conversion into chloride and chlorate on standing, and this action takes place rapidly on heating in the absence of free alkali:

$$3KClO = 2KCl + KClO_3.$$

Hence when chlorine in excess is passed into a hot solution of caustic alkali, the final product is a mixture of a chloride and chlorate.

It was, however, long ago shown by Gay-Lussac[1] that the formation of chlorate takes place far less rapidly even at high temperatures when free alkali is present, and Foerster and Jorre[2] have proved that when the solution of the alkali is treated with insufficient chlorine for its complete neutralisation, the hypochlorite solution formed is very stable at the ordinary temperature, and only undergoes slow conversion into chlorate on heating, whereas if chlorine be added in the slightest excess, or the liquid acidified, the conversion is very rapid, and is facilitated by heat or exposure to daylight. The formation of chlorates only appears to take place in presence of free hypochlorous acid, which acts on the chloride and hypochlorite present with formation of these salts. Aqueous hypochlorous acid is only very slightly dissociated into its ions, whereas the hypochlorites and chlorides yield the ions $\overline{ClO}$ and $\overline{Cl}$, and the formation of chlorates is attributed by Foerster to the action of these ions on the free hypochlorous acid.

189 *Electrolytic Production of Hypochlorites.*—As already mentioned under chlorine (p. 175), solutions of the alkali chlorides are decomposed by electrolysis into the metal and chlorine. In the absence of special precautions the former at once acts on the water, forming hydrogen and caustic alkali, and if this comes in contact with the chlorine evolved, interaction occurs with formation of hypochlorite and chlorate.[3] The primary product

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[1] *Compt. rend.* 1842, **14**, 27; *Annalen*, 1842, **43**, 153.

[2] *J. pr. Chem.* 1899 [2], **59**, 53.

[3] Foerster, *Zeit. anorg. Chem.* 1899, **22**, 1, 33; Vaubel, *Chem. Zeit.* 1898, **22**, 331; Borchet, *Compt. rend.* 1900, **134**, 718, 1340, 1624; Foerster and Müller, *Zeit. Electrochem.* 1902, **8**, 633, 655.

is hypochlorite, and according to Foerster, after a certain concentration is reached, this is partly converted into free hypochlorous acid in the neighbourhood of the anode by the action of the chlorine evolved, chlorate being then formed by the action of the free hypochlorous acid on the chloride and hypochlorite also present. At high temperatures the final product consists almost exclusively of chlorates, and this method is now largely employed for the commercial production of these salts.

CHLOROUS ACID AND THE CHLORITES.

190 This acid, like chlorine trioxide, is not known in the free state, but the chlorites can be prepared by adding potassium hydroxide to an aqueous solution of chlorine peroxide, a mixture of potassium chlorate, and potassium chlorite, $KClO_2$, being obtained[1]; if sodium peroxide be used instead of potassium hydroxide, oxygen is evolved and sodium chlorite formed[2]:—

$$Na_2O_2 + 2ClO_2 = 2NaClO_2 + O_2.$$

The chlorites of the alkali metals are soluble in water, and from their solutions the insoluble, or sparingly soluble, chlorites of silver, $AgClO_2$, and of lead, $Pb(ClO_2)_2$, may be prepared by double decomposition, as yellow crystalline powders. All the chlorites are very easily decomposed. Thus if the lead-salt be heated for a short time to 100°, it decomposes with detonation; and if it be rubbed in a mortar with sulphur or certain metallic sulphides, ignition occurs. The soluble chlorites possess a caustic taste, and bleach vegetable colouring matters, even after addition of arsenious acid. This latter reaction serves to distinguish them from the hypochlorites.

CHLORINE PEROXIDE. ClO_2.

191 This gas was first prepared and examined by Davy in 1815, and was obtained by him by the action of strong sulphuric acid on potassium chlorate. In preparing this substance special precautions must be taken, as it is a highly explosive and dangerous body.

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[1] Garzarolli-Thurnlackh and v. Hayn, *Annalen*, 1881, **209**, 203.

[2] Reychler, *Bull. Soc. chim.* 1901 [3], **25**, 659.

Preparation.—Pure powdered potassium chlorate is for this purpose thrown little by little into concentrated sulphuric acid contained in a small retort. After the salt has dissolved, the retort is gently warmed in warm water. In this reaction chloric acid is in the first instance liberated, and then decomposes as follows into perchloric acid, chlorine peroxide and water; thus:—

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

A convenient way of preparing a dilute solution of the peroxide is to float a dish, containing potassium chlorate and dilute sulphuric acid, on water contained in a larger dish, the whole being covered by a bell-jar. Chlorine peroxide is given off from the chlorate, and dissolves in the water in the large dish.[1]

Properties.—Chlorine peroxide must be collected by displacement, as it decomposes in contact with mercury and is soluble in water; it is a heavy, dark yellow gas, possessing a peculiar smell, resembling that of chlorine and burnt sugar. When exposed to cold the gas condenses to a dark-red liquid, which boils[2] at +9°, and freezes at −79° to an orange-coloured crystalline mass. Its vapour density corresponds to the formula ClO_2,[3] and the double formula, Cl_2O_4, previously employed is therefore incorrect. The gaseous, and especially the liquid and solid peroxide undergo sudden decomposition, frequently exploding most violently, hence their preparation requires extreme care, although, according to Schacherl, liquid chlorine peroxide may be distilled without decomposition if every trace of organic matter be excluded.[4]

Chlorine peroxide can be preserved without change in the dark; it is, however, slowly decomposed into its elementary constituents when exposed to light, and this decomposition takes place quickly and with explosion when an electric spark is passed through the gas, one volume of the gas yielding half a volume of chlorine and one of oxygen.

When phosphorus, ether, sugar, or other easily combustible substances are thrown into the gas they take fire spontaneously. This oxidising action of chlorine peroxide is well illustrated by the following experiments. About equal parts of powdered

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[1] Reychler, *Bull. Soc. chim.* 1901 [3], **25**, 659; see also Calvert and Davies, *Journ. Chem. Soc.* 1850, 193.

[2] Pebal, *Annalen*, 1875, **177**, 1.

[3] Pebal and Schacherl, *Annalen*, 1882, **213**, 113.

[4] *Annalen*, 1881, **206**, 68.

white sugar and potassium chlorate in powder are carefully mixed together with a feather on a sheet of writing paper, the mixture then brought on a plate or stone placed in a draught chamber, and a single drop of strong sulphuric acid allowed to fall upon the mixture, when a sudden ignition of the whole mass occurs. This is caused by the liberation of chlorine peroxide, which sets fire to a particle of sugar, and the ignition thus commenced quickly spreads throughout the mass, and the sugar is all burnt at the expense of the oxygen of the chlorate. The combustion of phosphorus can be brought about under water by a similar reaction: for this purpose some crystals of potassium chlorate and a few small lumps of yellow phosphorus are thrown into a test glass half filled with water, and a small quantity of strong sulphuric acid allowed to flow through a tube funnel to the lower part of the glass where the solids lie. As soon as the acid touches the chlorate, chlorine peroxide is evolved, and this gas on coming in contact with the phosphorus oxidises it, and bright flashes of light are emitted. When a drop of a solution of phosphorus in carbon bisulphide is allowed to fall on to a small quantity of powdered potassium chlorate, a loud explosion occurs as soon as the carbon bisulphide has evaporated.

Water at 4° dissolves about twenty times its volume of chlorine peroxide gas, forming a bright yellow solution, whilst at lower temperatures a crystalline hydrate is produced. If this aqueous solution be saturated with an alkali, a mixture of chlorite and chlorate is formed;

$$2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O.$$

When potassium chlorate is treated with hydrochloric acid a yellow gas is evolved, first prepared by Davy, considered by him to be a distinct oxide of chlorine, and termed *Euchlorine*. It has, however, been shown by Pebal[1] that this body is a mixture of free chlorine and chlorine peroxide in varying proportions. This mixture possesses even more powerful oxidising properties than chlorine itself, and is therefore sometimes used as a disinfectant.

[1] *Annalen*, 1875, **177**, 1.

CHLORIC ACID. $HClO_3$.

192 Chloric acid is the most important member of the series of chlorine oxy-acids. It was discovered by Berthollet in 1786, and is formed when the lower acids or aqueous solutions of the oxides of chlorine are exposed to light.

Preparation.—Chloric acid is best prepared by decomposing barium chlorate with an equivalent quantity of pure dilute sulphuric acid (Gay-Lussac, 1814);

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

The clear solution of chloric acid must be poured off from the deposited precipitate of barium sulphate, and carefully evaporated *in vacuo* over strong sulphuric acid. The residue thus prepared contains forty per cent. of pure chloric acid corresponding to the formula $HClO_3 + 7H_2O$. When attempts are made to concentrate the acid beyond this point, the chloric acid undergoes spontaneous decomposition with rapid evolution of chlorine and oxygen gases, and formation of perchloric acid. Chloric acid can also be prepared by decomposing potassium chlorate with hydrofluosilicic acid, H_2SiF_6, when insoluble potassium fluosilicate, K_2SiF_6, is precipitated, and the chloric acid remains in solution together with an excess of hydrofluosilicic acid. This can be removed by the addition of a little silica and by subsequent evaporation, when the fluorine passes away as gaseous tetrafluoride of silicon, SiF_4, and the pure chloric acid can be poured off from the silica, which settles as a powder to the bottom of the vessel.

Properties.—The acid obtained in this way in the greatest state of concentration does not rapidly undergo change at the ordinary temperature, but it forms perchloric acid on standing for some time exposed to light. Organic bodies such as wood or paper decompose the acid at once, and are usually so rapidly oxidised as to take fire. Aqueous chloric acid is colourless, possesses a powerful acid reaction and a pungent smell, and bleaches vegetable colours quickly. It is a monobasic acid, that is, it contains only one atom of hydrogen capable of replacement by a metal, with the formation of salts.

193 *The Chlorates.*—Of these salts potassium chlorate, $KClO_3$,

is the most important. It is easily formed by passing chlorine in excess into a hot solution of caustic potash (p. 344); thus:—

$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$

The chlorate is much less soluble in water than the chloride formed at the same time, so that by concentrating the solution the chlorate is deposited in tabular crystals, which may be purified from adhering chloride by a second crystallisation. Other chlorates can be prepared in a similar way; thus, for instance, calcium chlorate is obtained by passing a current of chlorine into hot milk of lime when the following reaction occurs:—

$$6Cl_2 + 6Ca(OH)_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

As mentioned on p. 344, chlorates are also prepared by the electrolysis of solutions of alkali chlorides.

All the chlorates are soluble in water, and many deliquesce on exposure to the air. The potassium salt is one of the least soluble of these salts, 100 parts by weight of water at 0° dissolving about 3·3 parts of this salt, whilst water at 15° dissolves twice this amount. By the action of reducing agents such as nascent hydrogen or sulphur dioxide, chlorates lose the whole of their oxygen and are converted into chlorides. A chlorate is recognised by the following tests:—

(1) Its solution yields no precipitate with silver nitrate, but on ignition the salt gives off oxygen gas, and a solution of the residual salt (a chloride) gives a white precipitate on addition of silver nitrate and nitric acid.

(2) To the solution of the chlorate a few drops of indigo solution are added, the liquid acidulated with sulphuric acid, and sulphurous acid (or sodium sulphite dissolved in water) added drop by drop. If a chlorate be present the blue colour is discharged, because the chloric acid is reduced to a lower oxide.

(3) Dry chlorates treated with strong sulphuric acid yield a yellow explosive gas (ClO_2).

The composition of the chlorates has been very carefully determined by Stas[1] and Marignac.[2] The following numbers

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[1] *Nouvelles Recherches Chimiques sur les Lois des Proportions*, 208.

[2] *Bibl. Univ.* **45**, 347.

give the percentage composition of silver chlorate according to the analyses of Stas :—

Chlorine	18·5257
Oxygen	25·0795
Silver	56·3948
	100·000

CHLORINE HEPTOXIDE. Cl_2O_7.

194 Chlorine heptoxide is prepared by dehydration of perchloric acid by means of phosphorus pentoxide, the latter being cooled in a retort below 10°, and perchloric acid slowly added, the mixture allowed to stand for some hours at a temperature below 10°, and then gradually warmed until the heptoxide distils over at 82°.

Properties.—Chlorine heptoxide is a colourless, volatile oil, boiling at 82° under ordinary pressure; on standing for two or three days it becomes greenish-yellow and evolves a greenish gas. It explodes very violently on percussion, or when brought into a flame, and great care must be taken in distilling it.

By the action of water it is converted into perchloric acid, whilst it dissolves in dry, well-cooled benzene, slowly attacking it. It reacts with iodine with liberation of chlorine, and formation of a white solid, which when heated under reduced pressure at 100°, leaves a residue of iodine pentoxide, giving off an oily liquid which dissolves in water, forming perchloric acid.[1]

PERCHLORIC ACID. $HClO_4$.

195 This acid was discovered by Stadion in 1816; it is formed by the decomposition of chloric acid on exposure to heat or light; thus:—

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$

It occurs in the form of its sodium salt, in small quantities in Chili-saltpetre.[2]

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[1] Michael and Conn, *Amer. Chem. J.* 1900, **23**, 444 : 1901, **25**, 89.

[2] Selckmann, *Zeit. angew. Chem.* 1898, 101. Fresenius and Bayerlein, *Zeit. anal. Chem.* 1898, **37**, 501.

It is best prepared from potassium perchlorate, which can be obtained in any quantity from the chlorate. We have already remarked, under oxygen, that when potassium chlorate is heated the fused mass slowly gives off oxygen, and a point is reached at which the whole mass becomes nearly solid, owing to the formation of perchlorate, the reaction,

$$4KClO_3 = 3KClO_4 + KCl$$

taking place concurrently with the decomposition of the chlorate into chloride and oxygen. The mass is then allowed to cool, powdered, and well washed with water, to remove the greater part of the chloride formed. In order to get rid of the unaltered chlorate the crystalline powder is gently heated with hydrochloric acid so long as chlorine and chlorine peroxide are evolved: a subsequent washing with water removes the remainder of the chloride, and the pure, sparingly-soluble perchlorate is left. Perchlorates are also formed by the electrolysis of solutions of chlorates under suitable conditions.[1]

Preparation.—In order to prepare perchloric acid, the pure dry potassium salt is distilled in a small retort with four times its weight of concentrated (previously boiled) sulphuric acid. At a temperature of 110° dense white fumes begin to be evolved, whilst a colourless or slightly yellow liquid, consisting of pure perchloric acid, $HClO_4$, distils over (Roscoe).[2] A better yield is obtained, however, if the distillation be carried out at 10–20 mm. pressure.[3] If the distillation be continued, this liquid gradually changes into a white crystalline mass, having the composition $HClO_4 + H_2O$. The formation of this latter body can be readily explained; a portion of the perchloric acid splits up during the distillation into the lower oxides of chlorine, oxygen and water, which latter combines with the acid already formed. When the crystalline hydrate is again heated it decomposes into the pure acid, which distils over, and into an aqueous acid which boils at 203°, and therefore remains behind in the retort. This reaction is employed in the preparation of the pure acid, $HClO_4$, as that obtained by the first preparation is generally rendered impure by sulphuric acid carried over mechanically.

An aqueous solution of the acid may be readily prepared by the addition of hydrofluosilicic acid to a solution of the

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[1] Foerster, *Zeit. Electrochem.* 1898, **4**, 386.

[2] *Journ. Chem. Soc.* 1863, 82.

[3] Michael and Conn, *Amer. Chem. J.*, 1900, **23**, 444.

potassium salt, and is sometimes used for the estimation of potassium.[1]

Properties.—Pure anhydrous perchloric acid is a volatile colourless liquid, which does not solidify when cooled in a mixture of ether and solid carbon dioxide;[2] it boils at 19° under 11 mm. pressure,[3] and has a specific gravity of 1·764 at 22°. It is strongly hygroscopic, quickly absorbing moisture from the air, and emitting dense white fumes of the hydrated acid. When poured or dropped into water it dissolves, combining with the water so vigorously as to cause a loud hissing sound and a considerable evolution of heat. A few drops thrown upon paper and wood cause an instantaneous and almost explosive inflammation of these bodies; and if the same quantity be allowed to fall upon dry charcoal, the drops decompose with an explosive violence which is almost equal to that observed in the case of chloride of nitrogen. If the pure acid, even in very small quantity, come in contact with the skin it produces a serious wound, which does not heal for months. Perchloric acid partially decomposes on distillation under atmospheric pressure the originally nearly colourless acid becomes gradually darker, until it attains the tint of bromine, and at last suddenly decomposes with a loud explosion. The composition of the substance which is here formed is unknown. The pure acid also undergoes spontaneous and explosive decomposition when preserved for some days even in the dark.[4] Iodine dissolves in it with the production of a yellow crystalline compound to which Michael and Conn [5] assign the composition HI_7O_3.

The methods employed in fixing the composition of this acid may here be referred to as illustrating the mode by which the quantitative analysis of similar bodies is carried out.

A quantity of the pure acid, $HClO_4$, is sealed up in a weighed glass bulb (Fig. 93) and the bulb and acid weighed. The sealed ends are then broken, the acid diluted with water, a slight excess of potassium carbonate solution being first added and then a slight excess of acetic acid, and the whole evaporated to dryness on the water bath. The residue is washed with absolute alcohol, which dissolves the potassium

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[1] *Zeit. angew. Chem.* 1893, 68.

[2] Vorländer and von Schilling, *Annalen*, 1900, **310**, 369.

[3] Michael and Conn, *loc. cit.*

[4] Vorländer and von Schilling, *loc. cit.*

[5] *Amer. Chem. J.* 1901, **25**, 89.

acetate, but has no action on potassium perchlorate; the latter remains behind and is weighed after drying. The weight thus found gives the amount of potassium salt yielded by a given weight of the pure acid. The potassium salt is then analysed, the oxygen being determined by the loss of weight which takes place on heating, the chlorine by dissolving the residue left on heating in water, precipitating with silver nitrate, and weighing the silver chloride formed, and the potassium by careful heating with an excess of sulphuric acid and weighing the potassium sulphate produced. In this manner it has been found that the acid and potassium salt have the composition represented by the formulæ, $HClO_4$ and $KClO_4$.

196 *Hydrates of Perchloric Acid.*—The monohydrate, $HClO_4 + H_2O$, whose mode of formation has been mentioned, is obtained in the pure state by the careful addition of water to the pure acid, $HClO_4$, until the crystals make their appearance. This substance, discovered by Serullas, was formerly supposed to be the pure acid; it melts at 50° and solidifies at this temperature again in colourless needle-shaped crystals, often several inches in length. The liquid emits dense white fumes on exposure to the air, and oxidises paper, wood, and other organic bodies with rapidity.

FIG. 93.

Van Wyk, from the melting-point curve of all mixtures of perchloric acid and water, concludes that there are four other hydrates of perchloric acid containing 2, 3, 4 and 6 molecules of water.[1]

As has been stated, the monohydrate decomposes at a higher temperature into the pure acid, and a thick oily liquid, which possesses a striking resemblance to sulphuric acid, boils at 203°, and has a specific gravity of 1·82. This liquid contains 71·6 per cent. of $HClO_4$, and does not correspond to any definite hydrate. An acid of the same composition, and possessing the same constant boiling point, is obtained when a weaker acid is distilled, the residue becoming more and more concentrated until the above composition and boiling point are reached. Aqueous perchloric acid, therefore, exhibits the same relations in this respect as the other aqueous acids.

[1] *Zeit. anorg. Chem.* 1902, **32**, 115.

Perchlorates.—Perchloric acid is a powerful monobasic acid, forming a series of salts, termed the perchlorates, which are all soluble in water, and a few of which are deliquescent. Potassium perchlorate, $KClO_4$, and rubidium perchlorate, $RbClO_4$, are the least soluble of the salts, one part of the former dissolving in 58, and of the latter in 92 parts of water at 21°. Both these salts are almost insoluble in absolute alcohol, and they may be, therefore, employed for the quantitative estimation of the metals.

The perchlorates are distinguished from the chlorates by the following reactions:—

(1) They undergo decomposition at a higher temperature than the chlorates.

(2) They are not acted upon by hydrochloric acid.

(3) They do not yield an explosive gas, ClO_2, when heated with strong sulphuric acid.

(4) They are not reduced to chlorides by sulphur dioxide.

197 *Constitution of the Oxy-acids of Chlorine.*—The constitution of these acids has frequently been the subject of discussion, and cannot as yet be regarded as definitely settled. On the assumption that chlorine always acts as a monovalent, and oxygen as a divalent element, the following formulæ are the only possible ones for these acids:—

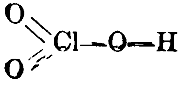
Hypochlorous acid, $H{-}O{-}Cl$.
Chlorous acid, $H{-}O{-}O{-}Cl$.
Chloric acid, $H{-}O{-}O{-}O{-}Cl$.
Perchloric acid, $H{-}O{-}O{-}O{-}O{-}Cl$.

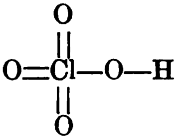
It has, however, been found, especially in the case of the carbon compounds, that substances containing oxygen atoms united together in this manner become more unstable as the number of oxygen atoms increases, whilst with the oxy-acids of chlorine the contrary is the case, hypochlorous acid being the most and perchloric acid the least unstable.

Another theory is that chlorine behaves as a monad in hypochlorous acid, a triad in chlorous acid, a pentad in chloric acid, and a heptad in perchloric acid, the constitutional formulæ being as follows:—

$Cl{-}O{-}H$

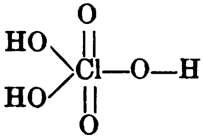
$O{=}Cl{-}O{-}H$





$$\mathrm{O}{=}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Cl}}}{-}\mathrm{O}{-}\mathrm{H}$$

This formula for perchloric acid readily explains the existence of the hydrate of perchloric acid, $HClO_4$, H_2O, the constitution of which would then be represented by the formula—



A substance possessing this formula should from analogy behave as a polybasic acid (compare the phosphoric acids), but hitherto no chemical or physical evidence of the polybasic nature of perchloric acid has been obtained, all the salts corresponding to the formula $HClO_4$, and the same holds true for chloric acid. On the whole, however, the balance of the evidence is in favour of the second view, which is also in agreement with the results obtained for periodic acid (p. 362).

Chlorine peroxide has been definitely proved to have the molecular formula ClO_2, and in this compound chlorine must be regarded as a tetrad; this fact is also in favour of the view that the valency of chlorine varies in its different compounds with oxygen.

OXYGEN AND BROMINE.

OXY-ACIDS OF BROMINE.

198 No compound of bromine and oxygen has as yet been obtained, but oxy-acids corresponding to those of chlorine are known; viz.:—

Hypobromous acid, $HBrO$.
Bromic acid, . . $HBrO_3$.

HYPOBROMOUS ACID, HBrO.

This acid and the corresponding salts, termed hypobromites, are formed, in a similar manner to hypochlorous acid, by the action of bromine on certain metallic oxides (Balard). Thus if bromine water be shaken up with mercuric oxide, and if the yellow liquid thus formed be treated successively with bromine and the oxide, a solution is obtained which contains in every 100 c.c. 6·2 grams of bromine combined as hypobromous acid, the reaction being as follows:—

$$HgO + 2Br_2 + H_2O = 2HOBr + HgBr_2.$$

The greater part of the hypobromous acid contained in this strong solution is decomposed on distillation into bromine and oxygen. It can, however, be distilled *in vacuo* at a temperature of 40° without undergoing this change.[1]

Aqueous hypobromous acid is a light straw-yellow coloured liquid, closely resembling in its properties hypochlorous acid, acting as a powerful oxidising agent and bleaching organic colouring matters.

If bromine be dropped very slowly into a cooled solution of an alkali hydroxide, a hypobromite is formed along with bromide, but it is very unstable, and changes quickly into bromate.[2]

By the action of bromine on lime, a substance similar to bleaching powder is formed, and this salt was formerly termed *bromide of lime.*[3]

BROMIC ACID, $HBrO_3$.

199 When bromine is dissolved in hot caustic potash or soda, a colourless solution is produced which contains a mixture of a bromide and a bromate; thus:—

$$3Br_2 + 6KHO = 5KBr + KBrO_3 + 3H_2O.$$

The sparingly soluble potassium bromate may be easily separated from the very soluble bromide by crystallisation. Potassium bromate is also formed when bromine vapour is passed into

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[1] Dancer, *Journ. Chem. Soc.* 1862, 477.

[2] Graebe, *Ber.* 1902, **35**, 2753.

[3] Berzelius, *Jahresb.* **10**, 130.

a solution of potassium carbonate which has been saturated with chlorine gas.

Solutions of alkali bromides are converted into bromates by electrolysis, the yield being almost quantitative if a little potassium chromate be added; in the case of the bromides of the alkaline earths some hypobromite is formed as well as bromate if the solution be kept cold.[1]

Preparation.—Free bromic acid is formed when chlorine is passed into bromine water; thus:—

$$Br_2+5Cl_2+6H_2O=2HBrO_3+10HCl.$$

The acid is, however, best obtained by the decomposition of the slightly soluble silver bromate. This salt is thrown down on the addition of silver nitrate to a solution of a soluble bromate; the precipitate thus prepared is well washed with water and then treated with bromine; bromic acid remains in solution and the insoluble silver bromide is thrown down;

$$5AgBrO_3+3Br_2+3H_2O=5AgBr+6HBrO_3.$$

Properties.—Obtained according to the foregoing methods, bromic acid is a strongly acid liquid reddening and ultimately bleaching litmus paper. On concentration at 100° the aqueous acid decomposes into bromine and oxygen, and it is at once decomposed by reducing agents such as sulphur dioxide and sulphuretted hydrogen, as also by hydrobromic acid, the following reactions taking place:—

$$(1)\quad 2HBrO_3+5SO_2+4H_2O=Br_2+5H_2SO_4.$$
$$(2)\quad 2HBrO_3+5SH_2=Br_2+6H_2O+5S.$$
$$(3)\quad HBrO_3+5HBr=3Br_2+3H_2O.$$

From a study of the velocity of the last reaction, Judson and Walker[2] have concluded that it takes place in stages.

Hydrochloric and hydriodic acids[3] decompose bromic acid in a similar manner with formation of the chloride or iodide of bromine.

The bromates are as a rule sparingly soluble in water, and decompose on heating into oxygen and a bromide, but no perbromate is formed in the process.

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[1] Müller, *Zeit. Elektrochem.* 1898, **5**, 469; Vaubel, *Chem. Zeit.* 1898, **22**, 231; Sarghel, *Zeit. Elektrochem.* 1899, **6**, 149, 173.

[2] *Journ. Chem. Soc.* 1898, 410.

[3] Noyes, *Zeit. physikal. Chem.* 1896, **19**, 599.

PERBROMIC ACID, $HBrO_4$.

This substance is stated by Kämmerer[1] to be formed by the action of bromine on dilute perchloric acid, the bromine liberating chlorine. Other observers have, however, failed to obtain the substance by this means, and the existence of the acid and of its salts is, therefore, more than doubtful.[2]

OXYGEN AND IODINE.

OXIDE AND OXY-ACIDS OF IODINE.

200 Only one oxide of iodine is known with certainty. This is the pentoxide I_2O_5, which unites with water to form iodic acid, HIO_3. Besides these, hydrated periodic acid, $HIO_4 + 2H_2O$, is known and hypoiodous acid HIO exists in solution.

HYPOIODOUS ACID. HOI.

201 When an aqueous solution of iodine is treated with freshly precipitated mercuric oxide a dilute solution of hypoiodous acid is formed,

$$HgO + 2I_2 + H_2O = HgI_2 + 2HOI,$$

whilst a more concentrated solution may be obtained by using a suspension of finely-divided iodine in water.[3]

Hypoiodous acid is very unstable and changes quickly into iodic and hydriodic acids, which react together to give free iodine and water.

A solution of iodine in water yields with alkali hydroxides a liquid possessing bleaching properties, and containing iodide, hypoiodite, iodate, and free iodine.[4] Hypoiodite and iodide are first formed,[5] the action being reversible, thus:—

$$2KOH + I_2 \rightleftarrows KI + KOI + H_2O.$$

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[1] *J. pr. Chem.* 1863, **90**, 190; Michael and Conn, *Amer. Chem. J.* 1901, **25**, 89.

[2] Muir, *Journ. Chem. Soc.* 1876, ii. 469; Wolfram, *Annalen*, 1879, **198**, 95; MacIvor, *Chem. News*, 1876, **33**, 35; 1887, **55**, 203.

[3] Taylor, *Chem. News*, 1897, **75**, 97; 1897, **76**, 17, 27; *Proc. Chem. Soc.* 1902, 72; *Mem. Manch. Phil. Soc.* 1902, **1**, 1; Orton and Blackmann, *Journ. Chem. Soc.* 1900, 830.

[4] *J. pr. Chem.* 1861, **84**, 385; Péchard, *Compt. rend.* 1899, **128**, 1453.

[5] Taylor, *Journ. Chem. Soc.* 1900, 725. See also Foerster and Gyr, *Zeit. Elektrochem.* 1903, **9**, 1.

The hypoiodite then changes slowly at ordinary temperatures, and rapidly on heating or in concentrated solution, into potassium iodide and iodate :—

$$3KOI = 2KI + KIO_3.$$

The formation of hypoiodite can easily be shown by dissolving a few crystals of iodine in 10 per cent. caustic potash, and immediately adding a few drops of this solution to manganese sulphate solution, when a dark brown precipitate of a higher oxide of manganese is formed; another portion of the caustic potash solution of iodine is then boiled and added to manganese sulphate, when a white precipitate of manganous hydroxide is produced, showing that the hypoiodite is no longer present, but has been changed into iodate.

Potassium hypoiodite is also formed by the action of iodine chloride on a solution of an alkali hydroxide,[1] thus:

$$6KOH + 3ICl = 3KOI + 3KCl + 3H_2O,$$

the hypoiodite changing gradually into iodide and iodate as above; with ammonia, however, the change is different, nitrogen iodide being produced.

Lunge and Schoch,[2] by the action of iodine on slaked lime and water at the ordinary temperature, obtained a substance having a peculiar odour, and resembling bleaching-powder in its general properties. It has probably the formula $CaOI_2$ or $Ca(OI)_2 + CaI_2$.

IODINE PENTOXIDE, I_2O_5, AND IODIC ACID, HIO_3.

202 This acid was discovered by Davy in the form of potassium iodate, which he obtained by the action of iodine on caustic potash; thus:—

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O.$$

Sodium iodate occurs in nature associated with sodium nitrate in Chili saltpetre, and iodic acid is not unfrequently met with in nitric acid prepared from this source.

Preparation.—(1) Free iodic acid is best obtained by dissolv-

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[1] Orton and Blackmann, *Journ. Chem. Soc.* 1900, 830.

[2] *Ber.* 1882, **15**, 1883.

ing powdered iodine in boiling concentrated nitric acid of sp. gr. 1·5, which oxidises it as follows:—

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

For this purpose 1 part of iodine is heated in a retort with 10–12 parts of the acid, a current of oxygen being passed through the acid throughout the process.[1] The solution is then evaporated and the residue heated to 200° until every trace of nitric acid is removed. The iodic acid thus loses water, and a white powder of iodine pentoxide, I_2O_5, is left. The latter can be obtained in colourless crystals by dissolving iodic acid in a mixture of sulphuric acid with a little fuming nitric acid at 200° and cooling.[2]

It is also formed by the action of chlorine heptoxide on iodine (see page 350). This oxide has a specific gravity of 4·487, and when heated to 300°, or subjected to the action of direct sunlight at ordinary temperatures, it is decomposed into oxygen and iodine.[3]

It is very soluble in water, dissolving with evolution of heat, and from the syrupy solution thus obtained rhombic crystals of iodic acid, HIO_3, are deposited.

(2) Iodic acid can also be obtained by the action of dilute sulphuric acid on barium iodate, which is prepared as follows: the requisite quantity of iodine is dissolved in a hot concentrated solution of potassium chlorate and a few drops of nitric acid added; immediately a violent evolution of chlorine gas commences, and, on cooling, the potassium iodate crystallises out. This salt is then dissolved in water and barium chloride added to the solution, when barium iodate separates out as a white powder.

(3) Iodic acid is likewise formed when chlorine is passed into water in which iodine in powder is suspended; thus:—

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

In order to separate the hydrochloric acid which is formed at the same time, precipitated oxide of silver is added until the acid is completely precipitated as the insoluble silver chloride.

(4) By the action of iodine on an aqueous solution of perchloric acid, iodic acid is formed and not periodic acid as was formerly stated.[4]

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[1] Scott and Arbuckle, *Journ. Chem. Soc.* 1901, 302.

[2] Chrétien, *Compt. rend.* 1896, **123**, 814.

[3] Berthelot, *Compt. rend.* 1898, **127**, 143, 795.

[4] Michael and Conn, *Amer. Chem. J.* 1901, **25**, 89.

Potassium iodate may also be obtained by very carefully heating a mixture of 2 mols. of potassium chlorate and 1 mol. of iodine, a simple substitution taking place,[1]

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2,$$

or by the electrolysis of potassium iodide in neutral solution in the presence of potassium chromate.[2]

Properties.—Crystallised iodic acid has a specific gravity at 0° of 4·629; it is insoluble in alcohol, but easily soluble in water. The concentrated aqueous solution boils at 104°,[3] and first reddens and then bleaches litmus paper. Phosphorus, sulphur, and organic bodies deflagrate when heated with iodic acid or with the pentoxide. Sulphur dioxide, sulphuretted hydrogen, and hydriodic acid reduce iodic acid with separation of iodine.

$$(1)\quad 2HIO_3 + 5SO_2 + 4H_2O = I_2 + 5H_2SO_4.$$
$$(2)\quad 2HIO_3 + 5H_2S = I_2 + 5S + 6H_2O.$$
$$(3)\quad HIO_3 + 5HI = 3I_2 + 3H_2O.$$

The first and third of these reactions have been proposed as methods for estimating periodates.[4]

203 *The Iodates.*—Iodic acid is a monobasic acid, and is distinguished from chloric acid and bromic acid by the fact that it forms not only the normal salts, but also acid salts. Thus the following potassium salts are known :—

Normal potassium iodate KIO_3.
Acid potassium iodate KIO_3, HIO_3.
Di-acid potassium iodate $KIO_3, 2HIO_3$.

The normal iodates are chiefly insoluble or sparingly soluble in water, the more soluble being those of the alkali metals. On heating, some iodates decompose into oxygen and the iodide of the metal, whilst others yield free iodine, oxygen, and the oxide, the latter sometimes undergoing further decomposition into the metal and oxygen. In some instances both reactions occur, a mixture of oxide and iodide remaining on ignition. In order to detect iodic acid, the solution, after acidifying with hydrochloric acid, is mixed with a small quantity of starch paste

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[1] Thorpe and Perry, *Journ. Chem. Soc.* 1892, 925.

[2] Müller, *Zeit. Elektrochem.* 1899, **5**, 469.

[3] Ditte, *Ann. Chim. Phys.* 1870, [4], **21**, 5.

[4] Vitali, *Boll. Chim. Pharm.* 1894, No. 4; *Apoth. Zeit.* 1894, **9**, 164.

and then an alkali sulphite or a solution of sulphurous acid is added drop by drop, thus liberating iodine which forms with the starch the blue iodide.

The constitution of iodic acid is not known with certainty. Unlike chloric acid it behaves as a polybasic acid, and the formula H-O-O-O-I, is therefore even more improbable than in the latter case. If, however, we assume that the iodine in this acid is pentavalent and ascribe to it the constitutional formula,  $\begin{matrix}O\\O\end{matrix}\!\!>I\text{-}O\text{-}H$, we are still unable to account for the existence of the acid and diacid salts mentioned above, except by regarding them as molecular compounds of the anhydrous salt and the acid. Thomsen[1] regards the molecular formula of the acid as $H_2I_2O_6$, and ascribes to it a constitutional formula in which the oxygen atoms are tetravalent, whilst another formula has been suggested by Blomstrand;[2] the evidence is, however, as yet insufficient to decide between the different suggestions.

Iodates form with molybdic, tungstic, and phosphoric acids[3] and with selenates[4] a number of compounds of a complex nature.

PERIODIC ACID, HIO_4.

204 This substance was discovered by Magnus,[5] and subsequently investigated by other chemists, especially by Ammermüller and Rammelsberg. Normal periodic acid, HIO_4, is not known. The hydrate, H_5IO_6 or HIO_4+2H_2O, is formed by the decomposition of silver periodate with bromine.

Iodic acid is converted into periodic acid when a 50 per cent. aqueous solution contained in a porous cell, immersed in dilute sulphuric acid, is electrolysed at 12°, the anode of lead coated with lead peroxide being placed in the iodic acid solution, and the cathode of platinum in the sulphuric acid.[6]

The hydrate is a colourless transparent crystalline deliquescent solid which melts at 133° and at 140° is completely decomposed into iodine pentoxide, water, and oxygen. The aqueous solution

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[1] *Ber.* 1874, **7**, 112. See also Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 40.

[2] *J. pr. Chem.* 1889, [2], **40**, 305.

[3] Chrétien, *Compt. rend.* 1896, **123**, 178.

[4] Weinland and Barttlingck, *Ber.* 1903, **36**, 1397.

[5] *Pogg. Ann.* 1833, **28**, 514.

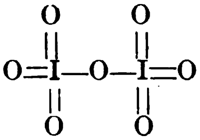
[6] Müller and Friedberger, *Ber.* 1902, **35**, 2652.

has a strong acid reaction and acts upon reducing agents in a similar way to iodic acid.

Periodic acid forms a remarkable series of salts, the composition of which at first sight seems somewhat complex. Thus there are said to exist salts having the following general formulæ, M representing a monad metal :—

$$MIO_4;\ M_4I_2O_9;\ M_3IO_5;\ M_8I_2O_{11};\ M_5IO_6;\ M_{12}I_2O_{13}.$$

If, however, we regard iodine as a heptad in these compounds, the hypothetical periodic anhydride, I_2O_7, would have the following constitutional formula :—



$$\mathrm{O{=}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{I}}}{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{I}}}{=}O}$$

The above salts may then be looked upon as derived from acids formed from this anhydride by union with varying numbers of molecules of water, in the manner shown below :—

$$\begin{aligned}
&I_2O_7 + H_2O = 2IO_3.OH = 2HIO_4\\
&I_2O_7 + 2H_2O = IO_2(OH)_2—O—IO_2(OH)_2 = H_4I_2O_9\\
&I_2O_7 + 3H_2O = 2IO_2(OH)_3 = 2HIO_4.2H_2O\\
&I_2O_7 + 4H_2O = IO(OH)_4—O—IO(OH)_4 = H_8I_2O_{11}\\
&I_2O_7 + 5H_2O = 2IO(OH)_5 = 2HIO_4,\ 4H_2O\\
&I_2O_7 + 6H_2O = I(OH)_6—O—I(OH)_6 = H_{12}I_2O_{13}\\
&I_2O_7 + 7H_2O = 2I(OH)_7 = 2HIO_4,\ 6H_2O.
\end{aligned}$$

No salts are known corresponding to the acid $I(OH)_7$, and the salts described as $M_8I_2O_{11}$ and $M_{12}I_2O_{13}$ appear not to be definite compounds,[1] but it will be seen that the compositions of the remaining acids correspond exactly with one or other of the series of salts. (Compare the constitution of the phosphoric acids.)

The best known series of periodates are those derived from the acids HIO_4, $H_4I_2O_9$, H_3IO_5, and H_5IO_6 which are termed *metaperiodates*, *diperiodates*, *mesoperiodates*, and *paraperiodates* respectively.

The periodates can be obtained in several ways; thus if chlorine be allowed to act on a mixture of sodium iodate and

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[1] Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 40.

caustic soda, a mixture of two sodium paraperiodates ($Na_2H_3IO_6$ and $Na_3H_2IO_6$) and sodium chloride is formed. Another method is to heat barium iodate, which is thus converted into barium periodate, iodine, and oxygen.

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$

The barium paraperiodate may be heated to redness without decomposition, whereas the other periodates are decomposed at this temperature with evolution of oxygen.

Potassium periodate can be formed by electrolysing a cold alkaline solution of potassium iodate in presence of potassium chromate, the best yield being obtained if an anode of lead peroxide be used.[1]

The periodates are, as a rule, but slightly soluble in water; their solutions give with silver nitrate and nitric acid a precipitate of silver periodate, a different silver salt being obtained according to the proportion of nitric acid present.[2] Like the iodates the periodates form double compounds with molybdic and tungstic acids.[3]

SULPHUR. $S = 31{\cdot}83$.

205 SULPHUR has been known from the earliest times as it occurs in the free or native state, in the neighbourhood of extinct as well as of active volcanoes. It was formerly termed Brimstone or Brennestone, and was considered by the alchemists to be the principle of combustibility, and believed by them to represent the alterability of metals by fire. The compounds of this element occur in nature in much larger quantities, and are much more widely distributed than free sulphur itself. The compounds of sulphur with the metals, termed *sulphides*, and those with the metals and oxygen, termed *sulphates*, are found in large quantities in the mineral kingdom. The more important compounds of sulphur occurring in nature are the following:—

(1) *Sulphides.* Iron pyrites FeS_2; copper pyrites $CuFeS_2$; galena PbS; cinnabar HgS; blende ZnS; grey antimony Sb_2S_3; realgar As_2S_2; orpiment As_2S_3.

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[1] Müller, *Zeit. Elektrochem.* 1904, **10**, 49.

[2] Kimmins, *Journ. Chem. Soc.* 1887, 356; 1889, 148.

[3] Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 40; Blomstrand, *Zeit. anorg. Chem.* 1892, **1**, 10.

(2) *Sulphates.* Gypsum $CaSO_4+2H_2O$; gypsum anhydrite $CaSO_4$; heavy spar $BaSO_4$; kieserite $MgSO_4+H_2O$; bitter spar $MgSO_4+7H_2O$; Glauber salt $Na_2SO_4+10H_2O$; green vitriol $FeSO_4+7H_2O$.

Volcanic gases almost always contain sulphur dioxide and sulphuretted hydrogen, and when these two moist gases come into contact they mutually decompose with the deposition of sulphur—

$$SO_2+2H_2S=3S+2H_2O.$$

It is very probable that native sulphur is, in some cases, formed by the above reaction. The apparatus shown in Fig. 94 serves to exhibit this change; the sulphuretted hydrogen gas evolved in the bottle (C) is passed into the large flask (A) into which is led at the same time sulphur dioxide from the small flask (B). The walls of the large flask are soon seen to become coated with a yellow deposit of sulphur.

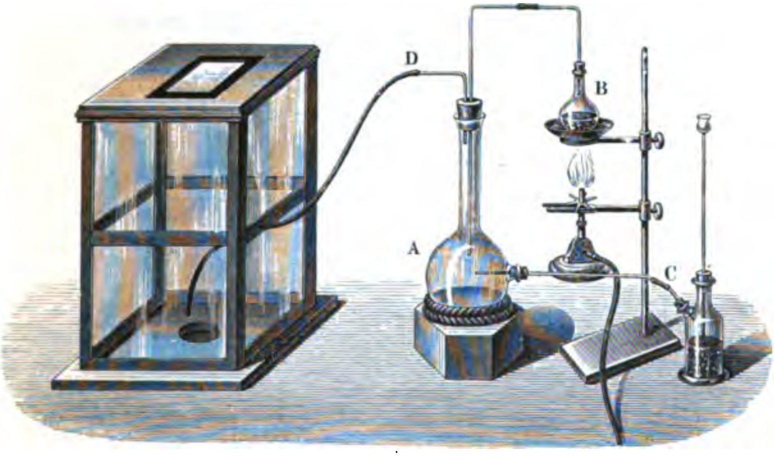

Fig. 94.

Sulphur compounds are also found widely distributed in the vegetable and animal world, in certain organic compounds such as the volatile oils of mustard and of garlic, and in the acids occurring in the bile. Sulphur is also found in small quantities in hair and wool, whilst it is contained to the amount of about 1 per cent. in all the albuminous substances which form so important a constituent of the animal body.

206 By far the largest proportion of the native sulphur of commerce comes from Italy, where it is found in the Romagna and in other parts of the country, but especially in very large quantities in the volcanic districts of the island of Sicily, where it occurs in widespread masses found chiefly on the south of the Madonia range stretching over the whole of the provinces of Caltanissetta and Girgenti, and over a portion of Catania. A very large number of distinct workings exist in Sicily, from which the annual production in the year 1900 amounted to 562,000 tons, of which only about 24,000 tons were imported into the United Kingdom. In recent years sulphur has also been produced in considerable quantity in Japan and the United States, the output of the former in the year 1900 being 14,435 tons, and of the latter 6,860 tons. It likewise occurs in the volcanic districts of Iceland and Mexico.

The deposits of Sicilian sulphur occur in the tertiary formation lying imbedded in a matrix of marl, limestone, gypsum, and celestine. The sulphur occurs partly in transparent yellow crystals termed *virgin sulphur* and partly in opaque crystalline masses to which the name of *volcanic sulphur* is given. Both these varieties are separated from the matrix by a simple process of fusion. The method often described, in which the sulphur ore is represented as being placed in earthenware pots in a furnace, the sulphur distilling out into other pots placed outside the furnace, appears to be unknown in Sicily. In the Romagna an apparatus made of cast-iron and provided with a receiver of the same material is employed, but in Sicily a very simple method of melting out the sulphur has long been, and still continues to be, in vogue. This old process consists in placing a heap of the ore in a round hole dug in the ground averaging from 2 to 3 metres in diameter and about one-half metre in depth. Fire is applied to the heap in the evening, and in the morning a quantity of liquid sulphur is found to have collected in the bottom of the hole; this is then ladled out, the combustion being allowed to proceed further until the whole mass is burnt out. By this process only about one-third of the sulphur contained in the ore is obtained, whilst the remaining two-thirds burns away evolving clouds of sulphurous acid.

This rough and wasteful process has been greatly improved by increasing the quantity of ore burnt at a given time, the excavation being made 10 metres in diameter, with a depth of 2½ metres, and so arranged (on the side of a hill, for instance) that an opening can be made from the lowest portion of the hole so that the sulphur, as it melts, may flow out. These holes are built up with masses of gypsum and the inside covered with a coating of plaster of Paris (see Fig. 95). The *calcaroni*, as these kilns are termed, are then filled with the sulphur ore which is built up on the top into the form of a cone, and air channels (b b b) are left in the mass by placing large lumps of the ore together. The whole heap is then coated over with powdered ore (c c), and this again covered with a layer of burnt-out ore, after which the sulphur is lighted at the bottom. By permitting the heat to penetrate very slowly into the mass, the sulphur is gradually melted, and running away by the opening (a) at the bottom of the heap, is cast into moulds. By this process, which takes several weeks to complete, the richest ores, containing from 30 to 40 per cent., may be made to yield from 20 to 25 per cent. of sulphur, whilst common ores, containing from 20 to 25 per cent., yield from 10 to 15 per cent. of sulphur, the remaining portion of the sulphur being used up for combustion.

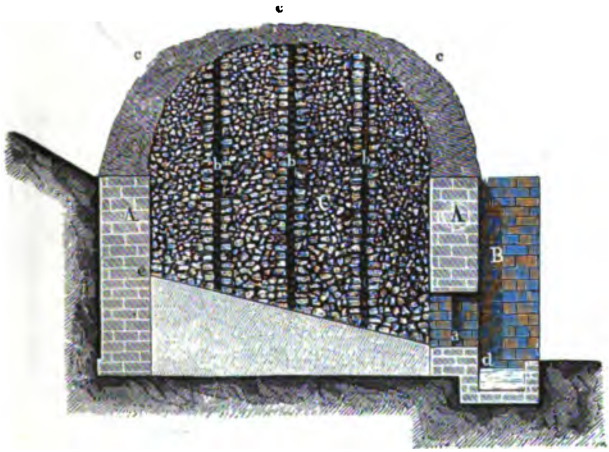

FIG 95.

For a long time, owing to the nature of the country and its inhabitants, very little advance was made on this wasteful process, but of late years the use of the Gill kiln, in which coke is used as fuel, has largely increased. This consists of a masonry oven, similar in form to, but smaller than the calcaroni, and is usually worked in batteries of two, four, or six "cells." After loading with fuel and ore, the first cell is lighted, and the gases force their way through side openings into the adjoining cell and heat up the charge previously placed in this; by the time the fusion in the first cell is complete the mass in the second cell is sufficiently hot to ignite spontaneously on admission of air, the gases as before then passing to a freshly charged cell. A much higher yield of sulphur is obtained in this manner, and in a much shorter time, whilst the emission of smoke and acid gases is much diminished.[1]

Other methods of recovery, such as extracting the sulphur with carbon bisulphide or other solvents, or by melting it out with high pressure steam, have not so far met with commercial success.

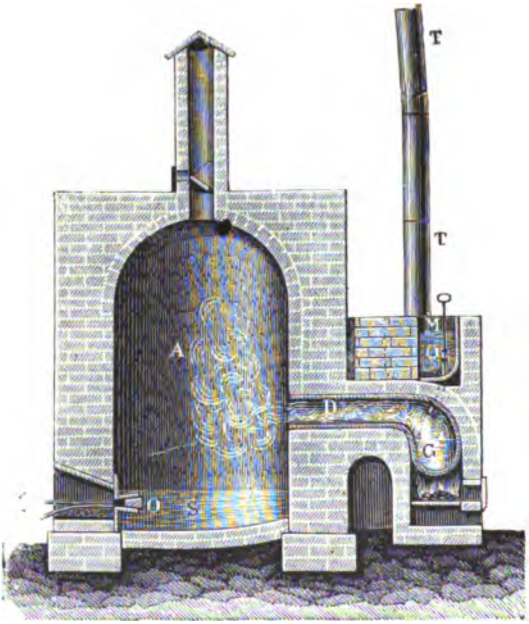

Fig. 96.

Fig. 97.

207 *Refining of Sulphur.*—Commercial Sicilian sulphur contains about 3 per cent. of earthy impurities which can be removed by distillation, an arrangement for this purpose being shown in Fig. 96. The sulphur is melted in an iron pot (M) and runs from this by means of a tube into the iron retort (G) where it is

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[1] *Chem. Trade Journ.* 1894, **14**, 320.

heated to the boiling point; the vapour of the sulphur then passes into the large chamber (A) which has a capacity of 200 cubic metres. In this chamber the sulphur is condensed, to begin with, in the form of a light yellow powder termed *flowers of sulphur,* just as aqueous vapour falls as snow when the temperature suddenly sinks below 0°. After a time the chamber becomes heated above the melting point of sulphur, and then it collects as a liquid which can be drawn off by means of the opening (O). It is then cast in slightly conical wooden moulds, seen in Fig. 97, and is known as *roll sulphur,* or *brimstone.* It is frequently also allowed to cool in the chamber and then obtained in large crystalline masses, known in the trade as block sulphur.

In France, Germany, and Sweden sulphur is also obtained by the distillation of iron pyrites, FeS_2. This method, which was described by Agricola in his work *De Re Metallica*, depends on the following decomposition of the pyrites:

$$3FeS_2 = Fe_3S_4 + S_2;$$

and the change which occurs is exactly similar to that by means of which oxygen is obtained from manganese dioxide:

$$3MnO_2 = Mn_3O_4 + O_2.$$

This decomposition of the pyrites is sometimes carried on in retorts, but more generally a kiln similar to a lime-kiln is employed for the purpose, having a hole at the side into which a wooden trough is fastened. A small quantity of fuel is lighted on the bars of the furnace, and then the kiln is gradually filled with pyrites; a portion of the sulphur burns away whilst another portion is volatilised; the burnt pyrites is from time to time removed from below, and fresh material thrown on the top, so that the operation is carried on uninterruptedly. In this way about half the sulphur which is contained in the pyrites can be obtained, whilst only about one-third of the total sulphur can be got by distilling in iron cylinders.

Sulphur is likewise obtained in this country, though in smaller quantities, as a by-product in the manufacture of coal-gas. The impure gas always contains sulphuretted hydrogen, which can be removed by passing the gas over oxide of iron, when a mixture of ferrous and ferric sulphides with free sulphur is formed:—

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O.$$
$$Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O.$$

These sulphides on exposure to air in presence of moisture are oxidised with separation of free sulphur, thus:—

$$Fe_2S_3 + 3O + H_2O = Fe_2O_3,H_2O + 3S;$$
$$2FeS + 3O + H_2O = Fe_2O_3,H_2O + 2S.$$

The mass can then be again employed for the purification of the gas, and this alternate oxidation and sulphurisation can be repeated until a product is obtained containing 50–60 per cent. of sulphur. The latter may be separated from the iron oxide by distillation or by treatment with carbon bisulphide in a suitable apparatus. In most cases, however, the spent oxide is employed for the manufacture of sulphuric acid, and is then burnt in kilns similar to those employed for burning pyrites.

Another and much more important source from which sulphur is now obtained is the residue or waste in the soda manufacture; this consists of calcium sulphide mixed with chalk, lime, and alkali sulphides. The sulphur which this material contains was formerly altogether wasted; now, however, it is economically regained in the alkali works on a very large scale. For this purpose the waste, which consists mainly of calcium sulphide, CaS, is treated in the presence of water with carbonic acid gas, calcium carbonate being thus produced whilst sulphuretted hydrogen is evolved:—

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S.$$

The gas thus obtained is then mixed with a quantity of air sufficient to supply the amount of oxygen required by the equation—

$$2H_2S + O_2 = 2H_2O + 2S,$$

and the mixture passed through a kiln known, from the name of its inventor, as a "Claus" kiln, where it comes in contact with heated ferric oxide and the above reaction takes place, the sulphur formed being condensed in cooling chambers, and recovered in the pure state.[1] A less pure sulphur is obtained in the same way from the sulphuretted hydrogen given off during the distillation of the ammoniacal liquor from gas works.

208 *Properties.*—Sulphur exists in several allotropic modifications. Thus it can be obtained in a number of different crystal-

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[1] Chance, *Journ. Soc. Chem. Ind.* 1888, **7**, 162.

line forms, and in at least two amorphous varieties, one of which is soluble and the other insoluble in carbon bisulphide. A form is also known which is soluble in water. *Rhombic* or *α-sulphur* occurs in nature in large yellow transparent octahedra. Fig. 98 (*a* and *b*) shows the form of the natural crystals of sulphur, which belong to the rhombic system, and have the following relation of the axes:—$a:b:c = 0{\cdot}8106:1:1{\cdot}898$. In addition to this primary form, no less than thirty different crystallographic modifications are known to exist in the case of sulphur. Crystals of rhombic sulphur have also been found in the sulphur chambers, having been deposited by slow sublimation. The specific gravity of this form of sulphur at 0° is 2·05–2·07; it is insoluble in water, very slightly soluble in alcohol, benzene, and ether, but dissolves readily in carbon bisulphide, chloride of sulphur, petroleum, and turpentine. Artificial crystals of sulphur are best obtained from solution in carbon bisulphide, which dissolves at the ordinary temperature about one-third of its weight of sulphur; the saturated solution on being allowed to evaporate slowly deposits large transparent octahedral crystals. Very well developed crystals can also be obtained by saturating pyridine with sulphuretted hydrogen gas and allowing the solution to stand exposed to the air for some time. The sulphuretted hydrogen is partially oxidised by the air, and the sulphur which is liberated crystallises out.[1] α-Sulphur melts at 114·5° (Brodie), forming a clear yellow liquid, which has a specific gravity of 1·803, and when quickly cooled, solidifies again at the same temperature; generally, however, it remains liquid at a temperature below its melting point, and then solidifies at a slightly lower temperature which varies with the point to which the liquid has been heated (see p. 375).

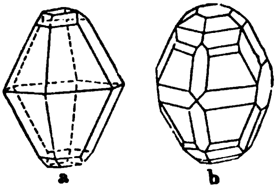

FIG. 98.

209 The second or *monoclinic modification*, known as β-

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[1] Ahrens, *Ber.* 1890, **23**, 2708.

sulphur, is obtained when melted sulphur is allowed to cool at the ordinary temperature until a solid crust is formed on the surface. The crust is then broken through, and the portion of sulphur still remaining liquid poured out; the sides of the vessel will then be found to be covered with a mass of long, very thin, transparent crystals having the form of monoclinic prisms (Fig. 99), the ratio of the axes of which is expressed by the following numbers:[1] $a:b:c = 1{\cdot}004:1:1{\cdot}004$. β-Sulphur appears to be trimorphous, since no less than three different types of crystals, all belonging to the monoclinic system, but having different axial ratios and optical properties, have been observed.[2]

Monoclinic sulphur has a specific gravity of 1·96, its melting-point is 119·25°, and, like the rhombic modification, it is readily soluble in carbon bisulphide.

210 According to the conditions under which the passage from the fused to the solid state takes place, sulphur may separate either in the form of rhombic or of monoclinic crystals. The rhombic crystals are obtained by placing about 200 grams of sulphur previously crystallised from solution in carbon bisulphide in a flask provided with a long neck, which is afterwards bent backwards and forwards several times to prevent the entry of floating dust. The sulphur is then melted by placing the flask in an oil bath heated to 120°, and when the contents are liquid the flask is immersed in a vessel filled with water at 95°. On standing for some time at a temperature of about 90°, crystals are seen to form, and when a sufficient quantity has been deposited the flask is quickly inverted; the portion of sulphur still liquid then flows into the neck and there at once solidifies, leaving the transparent rhombic crystals in the body of the flask.

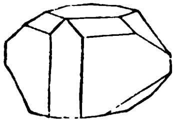

FIG. 99.

When a large mass of molten sulphur is allowed to cool slowly, rhombic crystals are also formed, and these cannot be

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[1] Mitscherlich, *Pogg. Ann.* 1832, **24**, 264.

[2] Muthmann, *Zeit. Kryst.* 1890, **17**, 336.

distinguished from the natural crystals. Thus Silvestri found such rhombic crystals 5 to 6 centimetres in length in a mass of sulphur which had been melted during a fire in a sulphur mine. When a transparent rhombic crystal of sulphur is heated for some time to a temperature above 97·6°, but below its melting-point, it becomes opaque when touched with a prismatic crystal, owing to its being converted into a large number of monoclinic crystals;[1] whereas, on the other hand, a transparent crystal of β-sulphur becomes opaque after standing for twenty-four hours at the ordinary temperature, having undergone a spontaneous change to the rhombic modification, the crystal having been converted into a large number of minute rhombic crystals. This conversion is accelerated by vibration, as, for instance, when the crystals are scratched, and also when they are exposed to sunlight; the change is always accompanied by an evolution of heat, 2·25 cal. being liberated by the conversion of 31·83 grams of the monoclinic into the rhombic variety. A saturated solution of sulphur in boiling carbon bisulphide deposits rhombic crystals on cooling, whilst, on the other hand, solutions in alcohol, ether, and chloroform give rise to the monoclinic crystals. A saturated solution in boiling benzene deposits the β-modification at temperatures between 75–80°, and the a-variety below 22°, whilst at intermediate temperatures mixtures of the two are formed. The "transition point" between rhombic and monoclinic sulphur is 95·5°, below which temperature the former and above it the latter is the stable form.[2]

Another crystalline form has been obtained by Engel[3] by extracting the aqueous solution of the sulphur soluble in water (p. 376) with chloroform, and allowing the latter to evaporate. The sulphur is thus obtained in orange yellow rhombohedra belonging to the hexagonal system which melt below 100°, and are denser than any other variety, having a sp. gr. of 2·135. On preservation they become opaque and pass into the form insoluble in carbon bisulphide. A further modification forming crystals belonging to the triclinic system has also been obtained by Friedel.[4]

211 *Amorphous sulphur* is known in two forms, one of which is soluble in carbon bisulphide and the other very nearly insoluble.

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[1] Gernez, *Compt. rend.* 1884, **98**, 810, 915; 1885, **100**, 1343; see also Findlay, "The Phase Rule" (Longmans, 1904, p. 31).

[2] Reicher, *Zeit. Kryst.* 1884, **8**, 593.

[3] *Compt. rend.* 1891, **112**, 866.

[4] *Bull. Soc. Chim.* 1879 (2), **32**, 114.

The soluble variety is produced by the decomposition of sulphuretted hydrogen water in the air and by the action of acids upon the polysulphides of the alkalis, &c.

Sulphur milk (*lac sulphuris*), a body known to the Latin Geber and now used as a medicine, is sulphur in this form. It is deposited as a fine white powder when two parts of flowers of sulphur are boiled with thirteen parts of water and one part of lime slaked with three parts of water, until the whole of the sulphur is dissolved. The reddish-brown solution thus prepared contains calcium pentasulphide, which is decomposed on the addition of hydrochloric acid with evolution of sulphuretted hydrogen and deposition of milk of sulphur; thus:—

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S.$$

The insoluble amorphous modification is known as *γ-sulphur*, and can be prepared in many different ways.

When melted sulphur is further heated, the pale yellow liquid first formed becomes more mobile until a temperature of 156–157° is reached, when the colour changes to a dark red and the viscosity rapidly increases, the liquid becoming so thick at 162° that it can hardly be poured out of the vessel, and reaching a maximum viscosity at 180°.[1] Observed in thin films, this change of colour from yellow to red is found to be associated with a distinct change in the absorption-spectrum, inasmuch as the absorption in the red gradually disappears, whilst that in the blue is gradually increased (Lockyer). If the temperature be raised still higher, the liquid becomes less viscid, although its dark colour remains, and on cooling down again the above-described appearances are repeated in inverse order. If the viscid sulphur be rapidly cooled, or if the more mobile liquid obtained at a higher temperature be poured in a thin stream into cold water, the sulphur assumes the form of a semi-solid transparent elastic mass, which can be drawn out into long threads. This is known as *plastic sulphur*; its condition is an unstable one, and on standing it gradually becomes opaque and brittle. The plastic variety of sulphur can be obtained by the arrangement shown in Fig. 100. The sulphur is first melted and then heated to its boiling point in the retort. The sulphur vapour condenses in the neck of the retort, and the liquid sulphur runs in a thin stream into cold water.

If the brittle mass be treated with carbon bisulphide a small

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[1] Brunhes and Dussy, *Compt. rend.* 1894, **118**, 1045.

portion, less than one per cent., dissolves, the remainder being left behind in the form of a dark-brown powder, the colour of which is due to small traces of fatty organic matter. In the absence of this the colour of the residue is lemon-yellow.

Together with the modification soluble in carbon bisulphide, "flowers of sulphur" contains a light yellow insoluble modification; and if a solution of sulphur in the above menstruum be exposed to the sunlight, a portion of the sulphur separates out in the insoluble form. The insoluble variety is also produced, accompanied by the soluble form, by the decomposition of chloride of sulphur with water, and in other similar reactions. On preservation it gradually changes into rhombic sulphur, and this transformation can also be produced by boiling it with alcohol or by subjecting it to a pressure of 8,000 atmospheres.[1]

FIG. 100.

The specific gravity of the insoluble variety, obtained from flowers of sulphur, is 1·9556 at 0°.

Whenever crystallised sulphur is heated above its melting point it is partially converted into the amorphous form, the amount of the latter depending on the temperature and length of time for which it is heated, and also on the nature of the other substances present. The quantity of amorphous sulphur formed is increased by passing dry air, sulphur dioxide, or hydrogen chloride through the liquid, or by adding phosphoric acid, but is decreased when nitrogen, carbon dioxide, sulphuretted hydrogen, or ammonia are employed.[2] The fact previously

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[1] Spring, *Ber.* 1881, **14**, 2579.

[2] Küster, *Zeit. anorg. Chem.* 1898, **18**, 365; Smith, *Proc. Roy. Soc. Edin.* 1902, **24**, 299, 342; Smith and Holmes, *Zeit. physikal. Chem.* 1903, **42**, 469.

mentioned (p. 371), that whenever sulphur is heated above its melting point it does not solidify until it has cooled below the latter temperature, appears to be due to this formation of amorphous sulphur, which dissolves in the molten liquid, lowering the freezing point of the solvent in the usual manner (p. 127). From the depression of the freezing point by different amounts of the amorphous variety, the latter appears to have the molecular formula S_8.

Colloidal or *δ-sulphur.*—According to Debus[1] an amorphous variety of sulphur which is soluble in water is contained in Wackenroder's solution (see Pentathionic acid). It forms a yellow, semi-liquid mass, and resembles colloidal silica in many of its properties. A variety which is also soluble in water is formed[2] when a saturated solution of sodium thiosulphate is decomposed by two volumes of hydrochloric acid which has been saturated at 25° and allowed to cool to 10°.

212 Sulphur boils, according to Regnault,[3] at 448·4°, and according to Callendar[4] at 444·53° under normal pressure; the vapour has an orange-yellow colour just above the boiling point, and assumes a deep red at 500°, which then becomes lighter, until at 650° it is straw-yellow.[5] The density of the vapour at 860–1040° was found by Deville and Troost[6] to be 2·23 (air = 1), corresponding to the molecular formula S_2. At a temperature of 524° Dumas[7] obtained a density of 6·56, corresponding to the molecular formula S_6. The later experiments of Biltz[8] have, however, shown that the vapour density has not this value through any range of temperature or pressure, but gradually decreases from 7·84 at 468° to 7·09 at 524°, and 4·73 at 606°, finally reaching the constant value 2·23. The vapour density at 440° under pressures varying from 540–125 mm. is, however, nearly constant, and is between that required by the molecular formulæ S_7 and S_8, but below 125 mm. it rapidly diminishes. Probably, therefore, at low temperatures the molecules S_8 are formed, which are dissociated as the temperature rises into diatomic molecules, and from the course of the curve repre-

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[1] Debus, *Journ. Chem. Soc.* 1888, i. 282.

[2] Engel, *Compt. rend.* 1891, **112**, 866.

[3] *Relation des Expériences*, tome 2.

[4] *Chem. News*, 1891, **63**, 1.

[5] Howe and Hamner, *J. Amer. Chem. Soc.* 1898, **20**, 757.

[6] *Ann. Chim. Phys.* 1857, [3] **50**, 172.

[7] *Ibid.* 1860, [3] **58**, 627.

[8] *Ber.* 1888, **21**, 2013; 1901, **34**, 2490. See also Bleier and Kohn, *Ber.* 1900, **33**, 50; *Monatsh.* 1900, **21**, 575.

senting the change of density with the pressure, it is not unlikely that S_6 and S_4 molecules are formed as intermediate products.[1] The molecular weight of sulphur in solution, as determined both by the freezing point and boiling point methods (p. 127), agrees approximately with that required by the formula S_8.

Sulphur ignites at 275–280° in oxygen, and at 363° in air,[2] burning with a pale blue flame which is much brighter in oxygen than in air. In this combustion sulphur dioxide is chiefly formed, but small quantities of the trioxide are also produced, and if the combustion be carried out in oxygen under 40–50 atmospheres pressure about one-half of the sulphur is converted into the latter oxide.[3] The heat of combustion of sulphur burning to gaseous sulphur dioxide is, according to Thomsen,[4] 71720 cal. for monoclinic, and 71080 cal. for rhombic sulphur.

A very slow combination of sulphur and oxygen also occurs at the ordinary temperature, and traces of sulphurous or sulphuric acid can be detected in sulphur after standing a few months in contact with moist air.

The flame of burning sulphur exhibits a continuous spectrum, but if a small quantity of sulphur vapour be brought into a hydrogen flame, a series of bright bands is seen when the blue cone in the interior of the flame is examined or when the sulphurised flame impinges on any cold surface. This blue tint is almost always seen when a pure hydrogen flame is brought for an instant against a piece of porcelain, the blue colour being produced, according to Barrett,[5] by the sulphur contained in the dust in the air. The absorption spectrum of sulphur has been obtained by Salet,[6] and the emission spectra, of which there are said to be two, a channelled-space and a line spectrum, have been mapped by Plücker and Hittorf,[7] and by Salet.[8] According to Lockyer two other spectra of sulphur occur, viz., a continuous absorption in the blue and a continuous absorption in the red. The change from the channelled-space spectrum to that showing absorption in the blue is observed when the vapour-density changes, the first of these

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[1] Preuner, *Zeit. physikal. Chem.* 1903, **44**, 733.

[2] Moissan, *Compt. rend.* 1903, **137**, 547.

[3] Hempel, *Ber.* 1890, **23**, 1455.

[4] *Thermochem. Untersuch.* **2**, 247.

[5] *Phil. Mag.* 1865, [4], **30**, 321.

[6] *Compt. rend.* 1872, **74**, 865.

[7] *Phil. Trans.* 1865, 1.

[8] *Compt. rend.* 1871, **73**, 559, 561, 742, 744. See also Watts's "Introduction to the Study of Spectrum Analysis" (Longmans, 1904, p. 28).

spectra being seen when the vapour possesses a normal density.

213 *Detection and Estimation of Sulphur.*—The simplest mode of detecting sulphur in a compound is to mix the substance with pure sodium carbonate, and fuse it before the blowpipe on charcoal, or, to avoid the introduction of sulphur from the gas flame, to mix the substance with sodium carbonate and charcoal, and heat in a small closed crucible. Sodium sulphide is thus formed, and this may then be recognised by bringing the fused mass on to a silver coin and adding water. The smallest quantity of sulphur can thus be recognised by the formation of a brown stain of silver sulphide. Sulphur is almost always quantitatively determined as barium sulphate. If the body is a sulphide, as, for instance, pyrites, it is finely powdered, and either fused with a mixture of sodium carbonate and nitre, the fused mass dissolved in water, and the filtrate, after acidifying by hydrochloric acid, precipitated with barium chloride; or the sulphide is oxidised with a mixture of nitric and hydrochloric acids or fuming nitric acid, the excess of acid removed by evaporation and barium chloride added, whereby insoluble barium sulphate is formed, and this, after washing and drying, is ignited and weighed. A further method is to fuse the mineral with 2 parts of caustic soda and 4 parts of sodium peroxide, the melt being then acidified and precipitated with barium chloride as above.[1]

Atomic Weight of Sulphur.—This has been determined by Berzelius, Dumas, Stas, and other chemists with closely concordant results. As a mean of five experiments Stas found that 100 parts of silver, when heated in sulphur vapour or in sulphuretted hydrogen, yielded 114·854 parts of silver sulphide; and as the mean of six others that 100 parts of silver sulphate, Ag_2SO_4, when heated in a current of hydrogen, left a residue of 69·203 silver. Hence when $O = 15·88$ and $Ag = 107·12$, the atomic weight of sulphur is 31·83.

SULPHUR AND HYDROGEN.

These elements unite to form at least two distinct compounds, viz., hydrogen mono-sulphide or sulphuretted hydrogen, H_2S, and hydrogen persulphide, the composition of which has not been ascertained with certainty.

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[1] Hempel, *Zeit. anorg. Chem.* 1893, **3**, 193.

SULPHURETTED HYDROGEN, OR HYDROGEN MONO-SULPHIDE.

H_2S. 33·83.

214 The preparation of a solution of the polysulphides of calcium by boiling lime with sulphur is described in the Papyrus of Leyden, the oldest chemical manuscript known (p. 4), and Zosimus frequently alludes to the unpleasant smell produced from this liquid, which was known to him as the "divine water" (Greek *θεῖον*, divine or sulphurous). The Latin Geber, moreover, described the preparation of milk of sulphur, but we do not notice either in his works or in those of the latter alchemists that any further mention is made of the fact that a fœtid smell is given off in the process. Not until we come to the writers of the sixteenth and seventeenth centuries do we find any description given of sulphuretted hydrogen, and then it is described under the general name of sulphurous vapours. Scheele was the first to investigate this compound with care. He found that it could be formed by heating sulphur in inflammable air, and he considered that it must be made up of sulphur, phlogiston, and heat.

Sulphuretted hydrogen is formed when hydrogen gas is passed through boiling sulphur, or when dry hydrogen gas is passed over certain heated sulphides. Thus, if a little powdered antimony trisulphide be placed in a bulb-tube and heated by a flame, and if a slow current of hydrogen be then passed over the heated sulphide, the escaping gas when allowed to bubble through a solution of lead acetate will produce a black precipitate of lead sulphide, thus showing the formation of sulphuretted hydrogen. The reaction is thus represented:—

$$Sb_2S_3 + 3H_2 = Sb_2 + 3H_2S.$$

It is also produced in the putrefactive decomposition of various organic bodies (such as albumin) which contain sulphur, and it is to the presence of this substance that rotten eggs owe their disagreeable odour. Sulphuretted hydrogen occurs, as has been stated, in volcanic gases, whilst certain mineral waters, such as those of Harrogate, contain dissolved sulphuretted hydrogen, which imparts to the waters their peculiar medicinal properties as well as their offensive smell.

215 *Preparation.*—(1) Sulphuretted hydrogen is best prepared by acting upon certain metallic sulphides with dilute acids; in

general, ferrous sulphide (sulphide of iron, obtained by melting together iron filings and sulphur) is employed for this purpose. Ferrous sulphide, FeS, dissolves readily in hydrochloric or in dilute sulphuric acid, sulphuretted hydrogen gas being liberated;

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$
$$FeS + 2HCl = H_2S + FeCl_2.$$

The apparatus shown in Fig. 101 may be used; the materials are placed in the large bottle and the gas which is evolved is washed by passing through water contained in the smaller one. When a regular evolution of gas for a long period is needed, the Kipp's apparatus, Fig. 102, is employed. The two glass globes (*a*) and (*b*) are connected by a narrow neck, whilst the tubulus of the third and uppermost globe (*c*) passes air-tight through the neck of (*b*). The sulphide of iron is placed in globe (*b*) and dilute sulphuric or hydrochloric acid poured through the tube-funnel until the lowest globe is filled and a portion of the acid has flowed on to the sulphide of iron. When it is desired to stop the current of gas, the stop-cock at (*e*) is closed, and the acid is forced by the pressure of the gas accumulating in the globe (*b*) up the tubulus into the uppermost globe (*c*).

FIG. 101.

More convenient arrangements, especially for use in laboratories, have been proposed in which only a small amount of acid is allowed to come in contact with the sulphide of iron at once, and is thoroughly used up in decomposing the sulphide, any excess of gas evolved being stored in a specially arranged vessel.[1]

(2) The gas thus obtained is, however, never pure, inasmuch as the artificial ferrous sulphide always contains some particles of metallic iron, and these coming into contact with the acid evolve hydrogen gas. Hence in order to prepare pure sulphuretted hydrogen, a naturally occurring pure sulphide, viz., antimony trisulphide, is employed, and this substance, roughly powdered, on being warmed with hydrochloric acid, evolves a regular current of the pure gas; thus:—

FIG. 102.

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

(3) A continuous current of sulphuretted hydrogen may likewise be obtained by heating a mixture of equal parts of sulphur and paraffin or vaseline (a mixture of hydrocarbons having the general formula C_nH_{2n+2}). By regulating the temperature to which the mixture is heated, the evolution of gas may be easily controlled. The exact nature of the changes which here occur remains as yet undetermined.[2]

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[1] Ostwald, *Zeit. anal. Chem.* 1892, **31**, 100; F. M. Perkin, *Journ. Soc. Chem. Ind.* 1901, 438.

[2] Galletly, *Chem. News*, 1871, **24**, 162; Prothière, *Journ. Chem. Soc.* 1903, ii. 284.

(4) In order to obtain a perfectly pure gas the artificially prepared sulphides of calcium or zinc may be decomposed by dilute acids, or a solution of magnesium hydrosulphide, $Mg(SH)_2$, may be heated at 60°, at which temperature it is decomposed.

216 *Properties.*—Sulphuretted hydrogen, as obtained by any of the above processes, is a colourless, very inflammable gas, possessing a sweetish taste and a powerful, very unpleasant odour resembling that of rotten eggs. It has a density of 1·1895 (air = 1), or slightly higher than that required by the formula H_2S. Under a pressure of 17 atmospheres the gas condenses to a colourless liquid, which boils under normal pressure at $-61·8°$ and freezes to a snow-white mass at $-85°$. The critical temperature of the gas is 100°, and the critical pressure 90 atm.[1] The liquid was first obtained in 1823 by Faraday, by allowing pure ferrous sulphide and sulphuric acid to act on one another in a strong bent sealed tube (p. 183).

The gas is soluble in water to a considerable extent, 1 vol. of the latter absorbing at 0° 4·37 vols. and at 15° 3·23 vols. of the gas, the solubility at temperatures between 2° and 43·3° being found from the equation—

$$C = 4·3706 - 0·083687t + 0·0005213t^2.$$

The gas is only slightly soluble at higher temperatures, and may therefore be collected over hot water.

The solution reddens blue litmus paper (whence the name *hydrosulphuric acid* has sometimes been given to the substance), and possesses the peculiar taste and smell of the gas. It soon becomes milky on exposure to air, oxygen combining with the hydrogen to form water whilst the sulphur separates out.

At $-18°$ sulphuretted hydrogen combines with water, forming a crystalline hydrate of the formula $H_2S + 7H_2O$.[2]

If inhaled even when diluted with large quantities of air, the gas acts as a powerful poison, producing insensibility and asphyxia. From the experiments of Thénard it appears that respiration in an atmosphere containing 1-800th part of its volume of sulphuretted hydrogen proves fatal to a dog, and smaller animals die when only half the above quantity is present. The best antidote is the inhalation of very dilute chlorine gas, as obtained by sprinkling bleaching-powder on a towel moistened with dilute acetic acid.

[1] Leduc, *Compt. rend.* 1897, **125**, 571.
[2] De Forcrand, *Compt. rend.* 1888, **106**, 1357.

When a light is brought to the open mouth of a jar filled with the gas it burns with a pale blue flame, the hydrogen uniting with the oxygen of the air to form water, and the sulphur burning partly to sulphur dioxide, and being partly deposited as a yellow incrustation on the sides of the jar. A mixture of two volumes of sulphuretted hydrogen and three volumes of oxygen explodes violently when an electric spark is passed through it, complete combustion taking place.

When heated by itself, the gas commences to decompose into its elements at 400°, and the dissociation is complete at a white heat. If a metal such as tin be heated in the gas, the whole of the sulphur combines with the metal, leaving the same volume of hydrogen, and this fact, taken in conjunction with the analysis and vapour density, shows that the molecular formula is H_2S.

Both as a gas and in solution in water sulphuretted hydrogen is converted into water and sulphur by nearly all oxidising agents, and even by strong sulphuric acid, so that this acid cannot be used for drying the gas:

$$H_2S + H_2SO_4 = S + 2H_2O + SO_2.$$

If two cylinders, one filled with chlorine and the other with sulphuretted hydrogen gas, are brought mouth to mouth, an immediate formation of hydrochloric acid gas and deposition of sulphur occurs. Fuming nitric acid dropped into a globe filled with sulphuretted hydrogen gas causes decomposition with explosive violence.

217 Both in the form of gas and as a solution in water, sulphuretted hydrogen is largely used in analytical operations as the best means of separating the metals into various groups, inasmuch as certain of these metals when in solution as salts, such as copper sulphate, antimony trichloride, &c., are precipitated in combination with sulphur as insoluble sulphides when a current of this gas is passed through an acid solution of the salt or mixture of salts:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

Certain other metallic salts are not thus precipitated because the sulphides of this second group of metals are soluble in dilute acids; thus sulphuretted hydrogen gas does not cause a precipitate in an acidified solution of ferrous sulphate, but if the acid be neutralised by soda or ammonia, a black precipitate of iron sulphide is at once thrown down:

$$FeSO_4 + H_2S + 2NaHO = FeS + Na_2SO_4 + 2H_2O.$$

Again, a third group of metals exists, the members of which are under no circumstances precipitated by the gas, their sulphides being soluble in both acid and alkaline solutions.

Many of the insoluble sulphides are distinguished by their peculiar colour and appearance, so that sulphuretted hydrogen is used as a qualitative test for the presence of certain metals as well as a means of separating them into groups.

The reaction of sulphuretted hydrogen on several metallic salt solutions may be exhibited by means of the apparatus seen in Fig. 103. The gas evolved in the two-necked bottle (A) passes through the several cylinders, and precipitates the sulphides of the metals whose salts have been placed in these cylinders; thus, B may contain copper sulphate, C antimony chloride, D a solution of zinc sulphate to which acid has been added, and E an ammoniacal solution of the same salt.

FIG. 103.

Many of the sulphides can also be obtained by the direct combination of the metal with sulphur. A class of bodies termed hydrosulphides is also known in which only half of the hydrogen of the sulphuretted hydrogen has been replaced. Thus, in addition to potassium sulphide, K_2S, we have potassium hydrosulphide, KHS, and in addition to calcium sulphide, CaS, which is insoluble in water, we have the soluble calcium hydrosulphide, $Ca(HS)_2$. Sulphuretted hydrogen therefore acts as a weak dibasic acid. The sulphides of the metals of the alkalis and alkaline earths also combine with sulphur forming unstable polysulphides such as K_2S_5, CaS_5.

Sulphuretted hydrogen immediately tarnishes silver with formation of black silver sulphide; hence it is usual to gild silver eggspoons to prevent them from becoming black by contact with the sulphuretted hydrogen given off from the albumin of the egg. Hence, too, silver coins become blackened when carried in the pocket with common lucifer matches.

HYDROGEN PERSULPHIDE.

218 This substance was first prepared by Scheele and afterwards more completely investigated by Berthollet and by Thénard,[1] and is best prepared by adding a clear, well cooled solution of the polysulphides of the alkalis or alkaline earths to dilute hydrochloric acid. Usually a solution of calcium pentasulphide is employed, which is obtained by boiling together 1 part of slaked lime, 2 parts of flowers of sulphur, and 16 parts of water. Hydrogen persulphide separates as a heavy, yellowish oil, which has a specific gravity of about 1·7, a characteristic pungent smell, and a very acrid and unpleasant taste. It dissolves readily in carbon bisulphide and benzene, but is scarcely soluble in alcohol.

It is a very unstable substance, gradually decomposing at the ordinary temperature with evolution of sulphuretted hydrogen, and liberation of free sulphur, which remains dissolved in the unaltered persulphide. On this account different investigators have obtained most varying percentages of sulphur in the oil, and its exact composition is somewhat doubtful. Rebs[2] has, however, found that the di-, tri-, tetra-, and pentasulphides of potassium, sodium, and barium all yield with acid an oil having approximately the composition H_2S_5, the yield being greatest when the pentasulphide is employed, and it seems therefore probable that this formula represents the composition of the yellow oil and not the formula H_2S_2 analogous to hydrogen dioxide. If, however, the oil be distilled under 40–100 mm. pressure, a colourless distillate is obtained which has a composition between those required by the formulæ H_2S_2 and H_2S_3, and

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[1] *Ann. Chim. Phys.* 1831, [2], **48**, 79.

[2] *Annalen*, 1888, **246**, 356.

this possibly consists of the disulphide containing a little dissolved sulphur.[1]

Like hydrogen dioxide, hydrogen persulphide rapidly reduces the oxides of gold and silver, ignition of the latter taking place (Odling). It dissolves phosphorus and iodine, gradually changing these substances respectively into phosphorus sulphide and hydriodic acid. On the other hand, it has no action on sulphur dioxide, differing in this respect essentially from hydrogen dioxide.

The alkaloid strychnine forms two distinct crystalline compounds with hydrogen persulphide, having the composition $C_{21}H_{22}N_2O_2+H_2S_3$ and $C_{21}H_{22}N_2O_2+H_2S_2$ respectively,[2] both of which on treatment with acids yield yellow oils with properties similar to the compound obtained in the manner described above.

SULPHUR COMPOUNDS WITH THE HALOGENS.

219 *Sulphur Hexafluoride,* SF_6.—Sulphur burns in fluorine at the ordinary temperature, forming a gaseous product consisting of a mixture of sulphur hexafluoride with smaller quantities of lower fluorides which have not been isolated. The hexafluoride is obtained in a pure condition by liquefying the mixed gases at 80°, fractionally distilling the liquid, removing the lower fluorides by shaking with aqueous caustic potash, and finally drying over anhydrous potash.[3] It is a colourless, inodorous, tasteless, incombustible gas, which is very sparingly soluble in water and freezes at $-55°$ to a white crystalline solid, which melts and boils at a slightly higher temperature. Unlike the other haloid derivatives of sulphur the hexafluoride is a very stable, chemically inert gas, comparable in this respect with nitrogen; it is not decomposed at a red-heat, and only partially so at the temperature of the induction spark. It is, however, rapidly attacked by boiling sodium, and when heated with sulphuretted hydrogen it is converted into hydrofluoric acid and sulphur. The analysis and vapour density agree with the molecular formula SF_6.

Sulphur Monochloride, S_2Cl_2.—This compound, the most stable of the chlorides of sulphur, is obtained as a dark yellow oily liquid by passing a current of dry chlorine gas over heated sulphur in the apparatus shown in Fig. 104. The sulphur is

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[1] Sabatier, *Compt. rend.* 1885, **100**, 1346, 1500.

[2] Hofmann, *Ber.* 1868, **1**, 81 ; Schmidt, *Ber.* 1875, **8**, 1267.

[3] Moissan and Lebeau, *Compt. rend.* 1900, **130**, 865.

placed in a retort and the chloride which distils over is collected in the cooled receiver. By rectification it can be obtained as a clear amber-coloured liquid possessing an unpleasant penetrating odour, having a specific gravity of 1·7055 (Kopp) and boiling at 138°. The density of its vapour is 4·70, corresponding to a molecular weight of 135·26, so that the compound contains two atoms of sulphur in the molecule, and has the formula S_2Cl_2, its exact molecular weight being 134·02. When thrown into water sulphur monochloride gradually decomposes with the formation of hydrochloric acid, thiosulphuric acid, and sulphur ; thus :—

$$2S_2Cl_2 + 3H_2O = 4HCl + 2S + H_2S_2O_3.$$

FIG. 104.

A number of other products, among which pentathionic acid may be named, are also formed by the further reaction of these substances. Metals decompose it on heating, with liberation of sulphur and formation of the chloride of the metal.

Sulphur dissolves in the monochloride so readily that the solution forms, at the ordinary temperature, a thick syrupy liquid containing 66 per cent. of sulphur. This property has been largely employed in the arts for the purpose of vulcanising caoutchouc.

Sulphur Dichloride, SCl_2.—A substance of this composition was supposed to be formed by passing chlorine into sulphur monochloride at the ordinary temperature, but it has been shown by Ruff and Fischer[1] that the product is in reality a

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[1] *Ber.* 1903, **36**, 418.

mixture of the mono- and tetrachlorides. Double compounds of this substance have, however, been obtained, namely, $AsCl_3, SCl_2$; C_2H_4, SCl_2; C_5H_{10}, SCl_2.

Sulphur Tetrachloride, SCl_4.—The existence of this compound was for a long time a matter of uncertainty, but Michaelis[1] has shown that it is formed when the monochloride is saturated with chlorine at – 22°. It is a mobile, yellowish-brown liquid, which at once evolves chlorine when removed from the freezing mixture. Double compounds of this substance with other metallic chlorides have been obtained, such as $2AlCl_3, SCl_4$; $SnCl_4, SCl_4$.

Sulphur Monobromide, SBr, or S_2Br_2, is best prepared by heating sulphur and bromine in equal molecular proportions at 100° in a sealed tube for two hours, and distilling the product under greatly reduced pressure. It is thus obtained as a garnet-red liquid, which freezes at –46°, boils at 57–58° under a pressure of 0·22 mm., and is rapidly decomposed by moisture. No evidence of the existence of higher bromides has been obtained.[2]

Sulphur Moniodide, S_2I_2.—When a mixture of iodine and sulphur in equal molecular proportions is dissolved in carbon bisulphide, and the latter allowed to evaporate, black rhombic tablets are obtained melting at 66·1–66·2°, the composition of which corresponds with the above formula; the same compound is formed by the action of sulphur monochloride on ethyl or propyl iodide.[3] The elements are only feebly combined, and the substance may possibly be a solid solution of sulphur and iodine.

SULPHUR AND OXYGEN.

Oxides and Oxyacids of Sulphur.

220 Sulphur forms with oxygen two compounds, which belong to the class of acid-forming oxides, and therefore, when brought into contact with water, both yield acids; thus:—

Sulphur dioxide, SO_2, yields Sulphurous acid, H_2SO_3.
Sulphur trioxide, SO_3, yields Sulphuric acid, H_2SO_4.

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[1] *Annalen*, 1873, **170**, 1.
[2] Ruff and Winterfeld, *Ber.* 1903, **36**, 2437.
[3] Linebarger, *Amer. Chem. J.* 1895, **17**, 33.

In addition to these we are acquainted with the oxides, S_2O_3 and S_2O_7, as well as with the following oxyacids of sulphur:

Hyposulphurous acid . . .	$H_2S_2O_4$.
Persulphuric acid	$H_2S_2O_8$.
Caro's acid	$H_2S_2O_9$.
Thiosulphuric acid	$H_2S_2O_3$.
Dithionic acid	$H_2S_2O_6$.
Trithionic acid	$H_2S_3O_6$.
Tetrathionic acid	$H_2S_4O_6$.
Pentathionic acid	$H_2S_5O_6$.
Hexathionic acid	$H_2S_6O_6$.

The names given to the last six acids are derived from θεῖον, Sulphur.

SULPHUR DIOXIDE. $SO_2 = 63$ 59.

221 The ancients were aware that when sulphur is burnt pungent acid smelling vapours are evolved. Homer mentions that the fumes from burning sulphur were employed as a means of fumigation, and Pliny states that they were employed for purifying cloth. For a long time it was thought that sulphuric acid was produced when sulphur was burnt, and it is to Stahl that we are indebted for first showing that the fumes of burning sulphur are altogether different from sulphuric acid, standing in fact half-way between sulphur and sulphuric acid, and therefore termed, according to the views of the time, phlogisticated vitriolic acid. Priestley in 1775 first prepared the pure substance in the gaseous state, to which the name of sulphurous acid was afterwards given.

When sulphur combines with oxygen the volume of sulphur dioxide formed is equal to that of the oxygen used, as may be seen by the following experiment. The apparatus employed, shown in Fig. 105, is similar in its arrangement to the syphon eudiometer previously described (p. 274), except that on one of the limbs a globe-shaped bulb has been blown, and this can be closed by a ground-glass stopper. This stopper is hollow, and through it are cemented two stout copper wires; one of these ends in a small platinum spoon, whilst to the other a small piece of thin platinum wire is attached, and this lies on the platinum spoon. A fragment of sulphur is then placed over the thin wire in the spoon, and the tube having been filled with oxygen gas, and the stopper placed in position, the sulphur is ignited by heating the wire with a current, care being taken to reduce the pressure on the gas by allowing mercury to run out by the tap, so as to avoid danger of cracking the globe. The eudiometer is then allowed to cool, when it will be found that the level of the mercury rises to the same point at which it stood before the experiment. Hence one molecule of sulphur dioxide contains one molecule or 31·76 parts by weight of oxygen, and therefore the molecule of the dioxide, which weighs

FIG. 105.

63·59, contains 31·83 parts, or one atom of sulphur, and its molecular formula is SO_2.

222 *Preparation.*—(1) Sulphur dioxide is formed not only by the combustion of sulphur, but also by the action of certain metals, such as copper, mercury, or silver, on concentrated sulphuric acid; thus:—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Sulphur dioxide is easily prepared for laboratory use by the above reaction. For this purpose a flask is half-filled with copper turnings or fine copper foil, and so much strong sulphuric acid poured in that the copper is not quite covered. The mixture is next heated until the evolution of gas commences; the lamp must then be removed, as otherwise the reaction may easily become too violent, and the liquid froth over.

(2) Pure sulphur dioxide is also produced when sulphur and sulphuric acid are heated together; thus:—

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

(3) It is also formed by the decomposition of a sulphite, such as commercial sodium sulphite, which, when treated with warm dilute sulphuric acid, easily evolves the gas; thus:—

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

A convenient method of employing this decomposition is to allow concentrated sulphuric acid to drop into a saturated solution of sodium bisulphite, which is now an article of commerce.

(4) Sulphur dioxide is made on the large scale for the preparation of the sulphites, especially of sodium sulphite and calcium sulphite, which are obtained by passing the gas either into a solution of caustic soda or into milk of lime. For this purpose charcoal is heated together with sulphuric acid, when carbon dioxide is evolved, together with sulphur dioxide; but the presence of the former compound for the purpose above mentioned is not detrimental; thus:—

$$C + 2H_2SO_4 = 2H_2O + CO_2 + 2SO_2.$$

The sulphur dioxide evolved in the roasting of certain metallic ores, which was formerly allowed to pass off into the atmosphere, is now frequently utilised for the preparation of the sulphites.

(5) Sulphur dioxide is used in enormous quantities for the manufacture of sulphuric acid. For this purpose it is chiefly obtained by roasting pyrites. When, however, especially pure sulphuric acid is needed, the dioxide is prepared by burning pure sulphur.

223 *Properties.*—Sulphur dioxide is a colourless gas, which occurs in nature in certain volcanic emanations, as well as in solution in volcanic springs. It possesses the well-known suffocating smell of burning sulphur. Its specific gravity is 2·2639 (Leduc),[1] and it can, therefore, be collected by downward displacement,

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[1] *Compt. rend.* 1893, **117**, 219.

like chlorine. If, however, the gas is required to be perfectly free from air, it must be collected over mercury. Sulphur dioxide does not support the combustion of carbon-containing material, and a burning candle is extinguished when plunged into the gas. Some of the metals, however, take fire when they are heated in the gas; thus, potassium forms the thiosulphate and sulphite, and tin and finely divided metallic iron are changed partly into sulphide and partly into oxide; lead dioxide, PbO_2, ignites when plunged into the gas and loses its brown colour, with formation of white lead sulphate, $PbSO_4$.

Sulphur dioxide is easily soluble in water, as is seen from the following table:[1]—

Temp.	1 vol. of water. dissolves SO_2.	1 vol. of the solution contains SO_2.
0°	79·789 vols.	68·861 vols.
20°	39·374 „	36·206 „
40°	18·766 „	17·013 „

The liquid consists of an aqueous solution of sulphurous acid, H_2SO_3, and reddens blue litmus paper, which the perfectly dry gas does not.

Sulphur dioxide condenses to a mobile liquid when exposed to pressure or cold. This liquid boils at −8°,[2] its vapour at 0° having a pressure of 1·16506 metres of mercury. The critical temperature is +155°·4 and the corresponding pressure 78·9 atmospheres. The condensation of this gas by pressure can easily be shown. For this purpose an ordinary but strong glass tube 20 mm. in diameter may be used; this is drawn out to a point at one end, whilst into the other end fits a greased caoutchouc plug, fastened on to an iron rod. The tube having been filled with the dry gas by displacement, the plunger is inserted, and the gas forcibly compressed; when the plunger has been driven down so that the gas occupies about one-fifth of its original bulk, drops of the liquid are seen to form and to collect in the drawn-out point. At a temperature above its boiling point, liquid sulphur dioxide evaporates quickly, absorbing much heat, the temperature sinking to −50° if a quick stream of air be driven through the liquid. If the liquid be placed under the receiver of an air-pump and the air rapidly withdrawn, evaporation takes place so quickly and so much heat

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[1] Bunsen und Schönfeld, *Annalen*, 1855, **95**, 2.

[2] Pierre, *Compt. rend.* 1870, **70**, 92.

is absorbed that a portion of the liquid freezes to a white snow-like mass melting at −76·1°. The formation of the solid may also be observed in the condensing tube when the plunger is quickly drawn out again. According to Cailletet and Matthias[1] its specific gravity at 0° is 1·4338, and it dissolves iodine, sulphur, phosphorus, resins, and many other substances which are insoluble in water.

In order to prepare liquid sulphur dioxide in larger quantity, the apparatus Fig. 106 is used. The gas evolved by the action of sulphuric acid on copper is purified by passing through the wash-bottle, and afterwards passes through the spiral glass tube, surrounded by a freezing mixture of ice and salt. The liquid which condenses and falls into the flask placed beneath may be preserved by sealing the flask hermetically where the neck has been drawn out. It may also be preserved in glass tubes provided with well-closing glass taps, the construction of one of which is seen in Fig. 107.

FIG. 106.

Sulphur dioxide, both in the gaseous state and in aqueous solution, exerts a bleaching action on vegetable colouring

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[1] *Compt. rend.* 1887, **104**, 1563.

matters. This fact was known to Paracelsus, and it is still made use of in the arts for bleaching silk, wool, and straw materials, which are destroyed by chlorine. The decolorising action of sulphur dioxide depends upon its oxidation in presence of water with formation of sulphuric acid, the hydrogen which is liberated uniting with the colouring matter to form a colourless body:

$$SO_2 + 2H_2O = H_2SO_4 + 2H.$$

Thus the bleaching action of this substance is a reducing one, whilst that of chlorine is an oxidising one. The colouring matter thus destroyed by bleaching with sulphur dioxide may often be restored when the cloth is exposed to the air, as in the case of linen marked with fruit stains, or when brought in contact with an alkali, as when bleached flannel is first washed with soap. The reducing action of sulphur dioxide is also made use of in paper manufacture, in order to get rid of the excess of chlorine left in the pulp after bleaching, when the following decomposition takes place:—

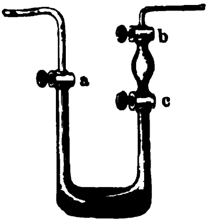

FIG. 107.

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

Sulphur dioxide is also a powerful antiseptic, and has been successfully employed for preventing the putrefaction of meat, as well as to stop fermentation. It is used in the sulphuring of wine, and also as a disinfecting agent.[1]

Sulphur dioxide has been shown by Tyndall to undergo a remarkable decomposition when exposed to light. If a beam of sunlight be passed through a long tube filled with the colourless gas a white cloud is seen to make its appearance, and this consists of finely divided particles of sulphur and sulphur tri-

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[1] Liquid sulphur dioxide is now manufactured by Messrs. Boake and Co., of Stratford, London, and stored in glass syphons or steel cylinders.

oxide, which are separated by the chemical action of the light. The gas is also slowly decomposed when a series of electric sparks is passed through it, into sulphur and sulphur trioxide, but this decomposition ceases when a certain quantity of the latter compound is formed, and can only be fully carried out when the trioxide is removed by allowing it to dissolve in strong sulphuric acid.

224 In order to detect sulphur dioxide some paper steeped in a solution of potassium iodate and starch is brought into the gas; this will at once be turned blue by the formation of the iodide of starch, if even only traces of the gas be present, iodine being liberated, as is shown by the following reaction:—

$$2KIO_3 + 5SO_2 + 4H_2O = I_2 + 2KHSO_4 + 3H_2SO_4.$$

An excess of sulphurous acid, however, will bleach the blue paper again with formation of hydriodic acid; thus:—

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

This last reaction serves as an excellent means of determining the quantity of sulphur dioxide present in solution. For this purpose a small quantity of starch paste is added to the solution, and then a standard solution of iodine is added by means of a burette to the solution until a permanent blue colour from the formation of iodide of starch is observed. It is, however, to be borne in mind that the above reaction does not take place unless the solutions are sufficiently dilute, for in concentrated solution sulphuric acid and hydriodic acid mutually decompose, forming free iodine, sulphurous acid, and water; thus:—

$$2HI + H_2SO_4 = I_2 + H_2SO_3 + H_2O.$$

Bunsen, who has investigated this subject thoroughly, finds that aqueous sulphurous acid can only be completely oxidised to sulphuric acid by means of iodine, when the proportion of sulphur dioxide does not exceed 0·04 to 0·05 per cent. of the solution. A standard solution of sulphurous acid may, of course, also be used for the quantitative determination of iodine, and Bunsen has made use of this reaction for the foundation of a general volumetric method. The principle of this method depends on the fact that a quantity of iodine, equivalent to that of the substance under examination, is liberated, and the quantity of this iodine is determined volumetrically by a dilute solution of sulphurous acid.[1]

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[1] *Journ. Chem. Soc.* 1856, 219.

SULPHUROUS ACID. H_2SO_3.

225 This substance, like many other acids whose corresponding anhydrides are gaseous, is only known in aqueous solution. This solution smells and tastes like the gas and has a strongly acid reaction. Exposed to the light it is decomposed with formation of pentathionic acid. When an aqueous solution saturated at 3° is allowed to stand, crystals of a hydrate, $H_2SO_3 + 6H_2O$, are obtained,[1] and other hydrates of the formulæ $H_2SO_3, 8H_2O$; $H_2SO_3, 10H_2O$; and $H_2SO_3, 14H_2O$ have been described. Sulphurous acid differs from the acids which have hitherto been described, inasmuch as it contains two atoms of hydrogen, both of which may be replaced by metals. It is therefore termed a *dibasic* acid; it forms two series of salts termed sulphites, in one of which only half of the hydrogen is replaced by a metal, and which may therefore be considered as being at once a salt and a monobasic acid, another in which the whole of the hydrogen of the acid has been replaced by a metal. The salts of the first series are termed *acid sulphites*, and of the latter *normal sulphites.*

The following serve as types of these different salts :—

Acid Sulphites, or Hydrogen Sulphites.	Normal Sulphites.
$HNaSO_3$	Na_2SO_3
$HKSO_3$	$KNaSO_3$
	$CaSO_3$

The acid sulphites of potassium and sodium are obtained by passing sulphur dioxide gas into caustic soda or caustic potash as long as it is absorbed. If, then, exactly the same quantity of alkali is added to this solution as was originally taken for the preparation, the normal salts are obtained. All the sulphites of the alkali metals are easily soluble in water, the normal sulphites of the other metals being either sparingly soluble or insoluble in water. They dissolve, however, in aqueous sulphurous acid and exist in such a solution as acid salts, but on evaporation they decompose with formation of the normal salt and sulphurous acid. The normal sulphites have no odour, and those which are soluble in water possess a sharp taste. They are readily detected by the fact that when they are mixed with dilute sulphuric acid

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[1] Geuther, *Annalen*, 1884, **224**, 219.

they give off sulphur dioxide, and also that their neutral solutions give a precipitate with barium chloride which is soluble in dilute hydrochloric acid, whereas if nitric acid be added to this solution and the mixture warmed, a precipitate of barium sulphate, formed by oxidation from the sulphite, is thrown down. Sulphurous acid also forms salts such as $Na_2S_2O_5$, which are known as *metabisulphites* or *metasulphites*, and other more complicated series, for an account of which the original memoirs must be consulted.[1]

The exact constitution of sulphurous acid has long been a matter of discussion, as two constitutional formulæ are possible.

$HO{\cdot}SO{\cdot}OH$	$H{\cdot}SO_2{\cdot}OH$
Sulphurous acid.	Sulphonic acid.

A substance of the first formula would be the true sulphur*ous* acid, in which the sulphur is present in a lower state of oxidation than in sulphur*ic* acid, $HO{\cdot}SO_2{\cdot}OH$, whilst an acid of the second constitution, differing from the latter by containing a hydrogen atom in place of a hydroxyl group, would be termed *sulphonic acid.* Derivatives corresponding to both these formulæ have long been known in which the hydrogen atoms are partly or wholly replaced by an alcohol radical, such as ethyl hydrogen sulphite, and ethylsulphonic acid, having respectively the formulæ:—

$$C_2H_5O{\cdot}SO{\cdot}OH \qquad\qquad C_2H_5{\cdot}SO_2{\cdot}OH$$

but no sufficient evidence was formerly available to show which of the above constitutional formulæ was possessed by the inorganic derivatives. It has, however, lately been proved that the sodium potassium sulphite, $NaKSO_3$, obtained by the action of caustic potash on sodium hydrogen sulphite is different from the salt of the same composition prepared by the addition of caustic soda to potassium hydrogen sulphite, as the two salts crystallise with different amounts of water of crystallisation, and yield different products when acted on by ammonium sulphide and ethyl alcohol. The existence of such "isomeric" salts cannot be accounted for by the first formula, but is in full agreement

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[1] Schwicker, *Ber.* 1889, **22**, 1728; Rörig, *J. pr. Chem.* 1888, [2], **37**, 250; Barth, *Zeit. physikal. Chem.* 1892, **9**, 176; Divers, *Journ. Chem. Soc.* 1886, 533; Hartog, *Compt. rend.* 1889, **109**, 436.

with the second, their constitution being represented by the formulæ :—

$K{\cdot}SO_2{\cdot}ONa$	$Na{\cdot}SO_2{\cdot}OK$
Sodium potassiosulphonate.	Potassium sodiosulphonate.

The salts of the alkali metals, therefore, and probably the other metallic sulphites, possess the sulphonic acid constitution, but as they have so long been known as sulphites this name is usually retained for them.

HALOGEN DERIVATIVES OF SULPHUROUS ACID.

226 *Thionyl fluoride*, SOF_2, is prepared by heating thionyl chloride with the equivalent quantity of arsenic trifluoride.[1] It is a colourless gas, which fumes slightly in moist air, has a suffocating odour, and on cooling condenses to a liquid boiling at $-32°$. It is decomposed by water with formation of hydrofluoric acid and sulphurous acids, and combines with ammonia to form the compounds $2SOF_2,5NH_3$, and $2SOF_2,7NH_3$.

Thionyl chloride, $SOCl_2$, is obtained by the action of phosphorus pentachloride on sodium sulphite (Carius),

$$Na_2SO_3 + 2PCl_5 = SOCl_2 + 2POCl_3 + 2NaCl,$$

or by adding sulphur trioxide to sulphur monochloride warmed to 75—80°,

$$SO_3 + S_2Cl_2 = SOCl_2 + SO_2 + S,$$

a continuous current of chlorine being passed through the mixture to reconvert the liberated sulphur into chloride, which then reacts with a further quantity of the trioxide.[2] It is also formed by the direct union of sulphur and chlorine monoxide, the temperature being maintained at $-12°$, as otherwise explosion may occur.[3]

It is a colourless highly refractive pungent liquid which fumes on exposure to air. It boils at 78° and has a specific gravity at 0° of 1·675. Like all other acid chlorides, when brought in contact with water it decomposes into its corresponding acid and hydrochloric acid :

$$SOCl_2 + 2H_2O = SO_3H_2 + 2HCl.$$

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[1] Meslans, *Bull. Soc. Chim.* 1896, [3], **15**, 391 ; Moissan and Lebeau, *Compt. rend.* 1900, **130**, 1436.

[2] *Journ. Chem. Soc.* 1903, ii. 420.

[3] Wurtz, *Compt. rend.* 1866, **62**, 460.

Thionyl bromide, $SOBr_2$, is formed by the action of thionyl chloride on potassium bromide,[1] and also together with *thionyl chlorobromide* by acting on the former with hydrogen bromide at 100°, both compounds being separated by fractional distillation under reduced pressure. The bromide is an orange-yellow liquid having a specific gravity of 2·61 at 0°, which boils at 68° under 40 mm. pressure, and readily decomposes at a higher temperature yielding sulphur dioxide, sulphur, and sulphur bromide. The chlorobromide forms a pale yellow liquid boiling with slight decomposition at 115° under atmospheric pressure, and having a specific gravity of 2·31 at 0°. Both compounds are quickly decomposed by water in a similar manner to thionyl chloride.[2]

SULPHUR TRIOXIDE. $SO_3, = 79·47$.

227 This body, which is called also sulphuric anhydride, and was formerly termed anhydrous sulphuric acid, is formed when a mixture of sulphur dioxide and oxygen is passed over heated platinum-sponge. In place of pure platinum-sponge, platinised asbestos may be employed; this is obtained by dipping some ignited asbetos into a tolerably concentrated solution of platinum chloride and then bringing it into a solution of sal-ammoniac. The insoluble double chloride of platinum and ammonium $(NH_4)_2PtCl_6$ is deposited on the threads of the asbestos, and when it has been dried and ignited this compound is converted into finely divided platinum.

In order to show the oxidation of sulphur dioxide to the trioxide the apparatus Fig. 108 may be employed. Sulphur dioxide is evolved in the flask (*a*) and is mixed in the wash-bottle, which contains strong sulphuric acid, with the oxygen from a gas-holder coming in through the tube (*b*). The mixture next passes through the cylinder (*e*) containing pumice-stone soaked in strong sulphuric acid in order to remove every trace of moisture, and then passes at (*c*) over the platinised asbestos. As long as this is not heated no change is observed; so soon, however, as it is gently ignited dense white fumes of the trioxide are formed which condense in a receiver (*d*), cooled by a freezing mixture, in the form of long white needles. In order to obtain these crystals, every portion of the apparatus must be

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[1] Hartog and Sims, *Chem. News*, 1893, **67**, 82.

[2] Besson, *Compt. rend.* 1896, **122**, 320.

absolutely dry; if even a trace of moisture be present the needles disappear at once, liquid sulphuric acid being formed. Wöhler has shown that instead of platinum, certain metallic oxides, such as copper oxide, ferric oxide, and chromic oxide, may be used.

A much more convenient method of preparing sulphur trioxide for experimental purposes is by the distillation of fuming sulphuric acid, which consists of a solution of the trioxide in .sulphuric acid, and is manufactured in large quantity. The writer known as Basil Valentine mentions that by this process a "philosophical salt" can be obtained, but the preparation of the "*sal volatile olei vitrioli*" from fuming acid was first described by Bernhardt in the year 1775.

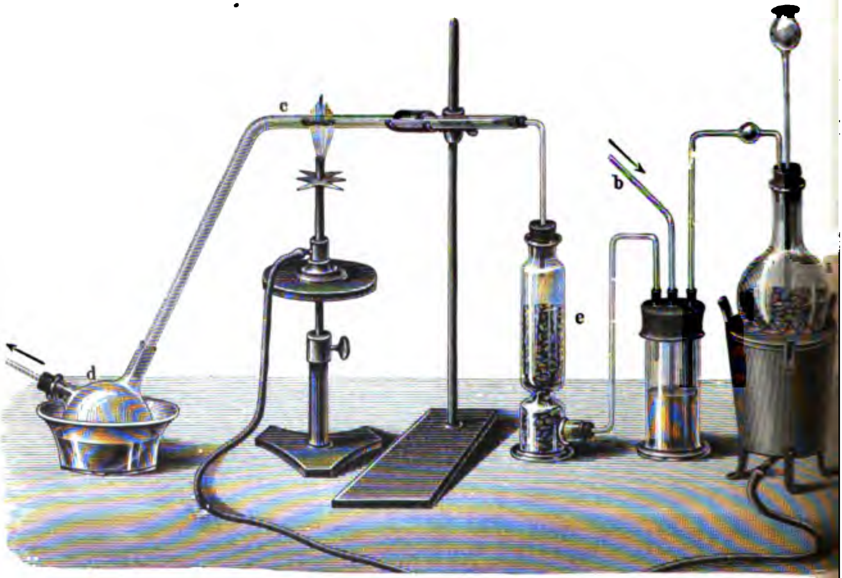

Fig. 108.

In order to prepare the trioxide, the fuming acid must be gently heated in a retort, and the trioxide collected in a well cooled and perfectly dry receiver, where it condenses in the form of long transparent colourless needles. The trioxide may also be obtained by the action of strong dehydrating agents, such as phosphorus pentoxide on sulphuric acid, or by heating certain anhydrous sulphates, as, for example, antimony sulphate.

228 *Properties.*—Sulphur trioxide exists in two polymeric modifications, known as the *a*- and *β*-trioxide. The *a*-trioxide,

obtained as described above, forms transparent prisms, which melt at 14·8° and solidify at the same temperature. The melted trioxide frequently remains liquid at temperatures much below this point, but solidifies on agitation, the temperature rising to 14·8°. It has a specific gravity of 1·97 at 20°, and its molecular weight, as determined by the freezing-point method in phosphorus oxychloride solution, corresponds to the formula SO_3.

When allowed to stand at temperatures below 25° it gradually changes into the β-modification, which forms aggregates of silky-white needles resembling asbestos, and on heating to 50° is slowly converted into the α-modification. Its molecular weight in phosphorus oxychloride solution corresponds to the formula S_2O_6. The chemical activity of this modification is much less marked than that of the α-trioxide.[1]

The trioxide absorbs moisture rapidly from the atmosphere, and evolves dense white fumes on exposure to the air, and when brought in contact with anhydrous baryta combines with it to form barium sulphate, $BaSO_4$, with such energy that the mass becomes incandescent.

The density of sulphur trioxide vapour is 2·75, showing that in the gaseous state it has the molecular formula SO_3, and this conclusion is confirmed by the fact that when the vapour is led through a red-hot tube two volumes yield two volumes of sulphur dioxide and one volume of oxygen.

Sulphur trioxide is now manufactured in very large quantities by the combination of sulphur dioxide and oxygen in presence of catalytic agents, such as platinum or ferric oxide The sulphur trioxide is, however, for the most part, at once converted into either sulphuric or fuming sulphuric acid, and the manufacture will therefore be described in connection with those acids.

SULPHURIC ACID. H_2SO_4.

229 Sulphuric acid is, without doubt, the most important and useful acid known, as by its means nearly all the other acids are prepared, whilst its manufacture constitutes one of the most important branches of modern industry owing to the great variety of purposes for which it is needed, as there is scarcely an art or a trade in which in some form or other it is not

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[1] Schultz-Sellack, *Ber.* 1870, **3**, 216; Oddo, *Gazzetta*, 1901, **31**, 158.

employed. It is manufactured on an enormous scale in many countries, and it is estimated that at present about 1,000,000 tons are annually produced in Great Britain alone, whilst Germany and the United States each produce nearly 900,000 tons.[1]

It appears probable that the Latin Geber was acquainted with sulphuric, or, as it was formerly called, vitriolic acid, in an impure state; but the writer known as Basil Valentine was the first fully to describe the preparation of this acid from green vitriol or ferrous sulphate, and to explain that when sulphur is burnt with saltpetre a peculiar acid is formed.

Originally, sulphuric acid was obtained exclusively by heating green vitriol according to a decomposition which we shall study hereafter; the acid thus prepared consists of sulphur trioxide dissolved in sulphuric acid, and from its property of fuming in the air is known as *fuming sulphuric acid.* The method by which the greater part of the acid is at present produced is said to have been introduced into England from the Continent by Cornelius Drebbel; but the first positive information which we possess on the subject is that a patent for the manufacture of sulphuric acid was granted to a quack doctor of the name of Ward.[2] For this manufacture he employed glass globes of about 40 to 50 gallons in capacity; a small quantity of water having been poured into the globe, a stoneware pot was introduced, and on to this a red-hot iron ladle was placed. A mixture of sulphur and saltpetre was then thrown into this ladle, and the vessel closed in order to prevent the escape of the vapours which were evolved. These vapours were absorbed by the water, and thus sulphuric acid was formed. This product, from the mode of its manufacture, was termed oil of vitriol made by the bell, as contradistinguished from that made from green vitriol, and it cost from 1*s.* 6*d.* to 2*s.* 6*d.* per lb.

Dr. Roebuck of Birmingham was the first to suggest a great improvement, in the use, instead of glass globes, of leaden chambers, which could be constructed of any wished-for size. Such leaden chambers were first erected in Birmingham in 1746, and in the year 1749 at Prestonpans in Scotland. The mode of working this chamber was similar to that adopted with the glass globes; the charge of sulphur and nitre was placed within the

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[1] For a complete account of the manufacture of sulphuric acid see Lunge's excellent treatise on the subject. Gurney and Jackson, London, 1903.

[2] See *Dossie's Elaboratory Laid Open*, 1758, Intro. p. 44.

chamber, ignited, and the door closed. After the lapse of a certain time, when the greater portion of the gases had been absorbed by the water in the chamber, the door was opened, the remaining gases allowed to escape, and the chamber charged again.

The leaden chambers first set up were only six feet square, and for many years they did not exceed ten feet square, but in these all the acid employed in the country was manufactured, whilst much was exported to the Continent, where the chamber acid still goes by the name of English sulphuric acid. The first vitriol works in the neighbourhood of London were erected at Battersea in the year 1772, by Messrs. Kingscote and Walker, and in 1783 a connection of the above firm established works at Eccles, near Manchester. This manufactory, the first erected in Lancashire, contained four chambers, each twelve feet square, and four others, each of which was forty-five feet long and ten feet wide.

In the year 1788 a great stimulus was given to the manufacture of sulphuric acid by Berthollet's application of chlorine, discovered by Scheele in 1774, to the bleaching of cotton goods, and, from that time to the present, the demand has gradually extended until it has become enormous and almost unlimited in extent.

The next improvement in the manufacture consisted in making the process continuous. The foundations of this mode of manufacture appear to have been laid by Chaptal, and the principle employed by him is that which is at the present day in use. The improvements thus proposed were (1) the introduction of steam into the chamber instead of water, (2) the continuous combustion of the sulphur in a burner built outside the chamber, (3) sending the nitrous fumes from the decomposition of nitre placed in a separate vessel, along with the sulphur dioxide gas and air into the chamber.

Many attempts were made during the last century to manufacture sulphuric acid by combining sulphur dioxide with oxygen in presence of catalytic substances such as platinum, and dissolving the sulphur trioxide formed in water, and as early as 1831 a patent for such a process was taken out by Peregrine Phillips. For many years no commercial success was obtained, but in 1875 processes were patented almost simultaneously by Squire and Messel in this country and by Winkler in Germany, according to which fuming sulphuric acid was manufactured at prices which allowed of competition with that produced from green vitriol. From about 1890 the quantity obtained by such "contact" processes has rapidly increased, chiefly owing to the demands for fuming sulphuric acid by the coal-tar colour manufacturers, and at the present time many thousand tons of sulphur trioxide are produced annually, largely at the German colour works. The fuming acid is thus obtained at a lower cost than by the green vitriol process, which has now been entirely abandoned, and it is also possible to prepare concentrated sulphuric acid by this process at least as cheaply as by the use of the leaden chamber, although for more dilute acids the latter method is still the cheaper one.

THE LEAD CHAMBER PROCESS.

230 The theory of the formation of sulphuric acid in the leaden chambers has long been the subject of discussion, and cannot yet be said to have been fully elucidated.[1] A large number of different reactions between the nitrous gases, sulphur dioxide, oxygen, and water present undoubtedly take place, resulting finally in the formation of sulphuric acid, but the exact nature of some of the reactions as well as the extent to which they occur is still a matter of doubt. It was recognised by Clément and Désormes as early as 1806 that the oxidation of the sulphur dioxide to sulphuric acid is not due solely to the oxygen contained in the nitrous gases introduced, but that the latter in some manner bring about the combination of the sulphur dioxide with the free oxygen always present, so that a small amount of nitrous gases in presence of water is able to bring about the formation of a large quantity of sulphuric acid.

The view of the mechanism of the reaction suggested by Berzelius may be simply expressed by saying that although sulphur dioxide in presence of water or steam is unable rapidly to absorb atmospheric oxygen, it is able to take up oxygen from such oxides of nitrogen as N_2O_3 or NO_2. If, therefore, these oxides are present in the chamber they give up part of their oxygen to the sulphur dioxide, and are reduced to nitric oxide,

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[1] For a complete discussion and bibliography of this subject see Trautz, *Zeit. physikal. Chem.* 1904, **47**, 513, and Lunge's *Sulphuric Acid and Alkali* (Gurney and Jackson, 1903), p. 750.

NO. This is, however, able to absorb free oxygen, and is at once reconverted into N_2O_3 or NO_2. This continuous reaction may be represented as follows:—

$$(1)\ NO_2+SO_2+H_2O=H_2SO_4+NO.$$
$$(2)\ NO+O=NO_2.$$

Another view, founded upon that of Davy, is due to Lunge According to him, nitrogen peroxide, NO_2, is not formed in the chambers, and is therefore not the essential agent which brings about the oxidation of the sulphur dioxide, nor does reduction to nitric oxide, NO, usually occur, the active substance being nitrogen trioxide, N_2O_3. In the first instance, the sulphur dioxide combines with nitrogen trioxide, oxygen, and water to form nitrosyl-sulphuric acid, $SO_2(OH)O{\cdot}NO$, according to the equation (1):—

$$(1)\ 2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)O.NO.$$
$$(2)\ 2SO_2(OH)O.NO + H_2O = 2H_2SO_4 + N_2O_3.$$

This substance on meeting with an excess of water vapour is decomposed into sulphuric acid which falls to the bottom of the chamber, and nitrogen trioxide which is ready to react again (equation 2). The existence of nitrosyl-sulphuric acid is well known to the manufacturers of sulphuric acid, since it is formed as a white crystalline substance when the supply of steam has been insufficient, and is termed by them "chamber crystals."

From the results of an investigation of the action of nitric acid on sulphurous acid and its salts Raschig[1] suggested an entirely different theory of the formation of sulphuric acid in the chambers. According to his view, the first reaction which takes place is that of orthonitrous acid, $N(OH)_3$, with sulphurous acid to form dihydroxylaminesulphonic acid, or the corresponding nitrososulphonic acid, $NO.SO_2.OH$, formed from it by loss of the elements of water, neither of which compounds has been isolated;

$$N(OH)_3 + H.SO_2OH=(OH)_2N.SO_2OH + H_2O.$$

This is then further decomposed by nitrous acid into sulphuric acid and nitric oxide,

$$(OH)_2N.SO_2OH + N(OH)_3 = 2NO + H_2SO_4 + 2H_2O,$$

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[1] *Annalen*, 1887, **241**, 242.

the nitric oxide then recombining with oxygen and water to form orthonitrous acid,

$$2NO + O + 3H_2O = 2N(OH)_3.$$

As, however, these reactions have not been experimentally carried out under conditions corresponding to those existing in the chambers, and the hypothetical dihydroxylaminesulphonic acid has not been isolated by any method, this theory has not received general acceptation as representing the means by which at any rate the great bulk of the sulphuric acid is produced. Raschig[1] has, however, recently published a further paper bringing forward further evidence in favour of his views.

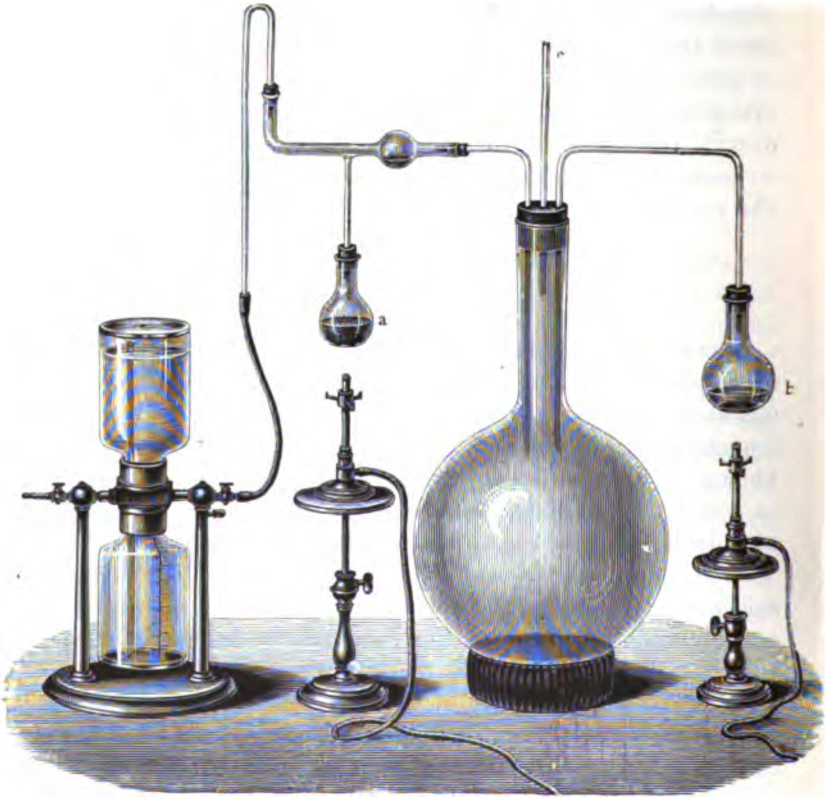

Fig. 109.

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[1] *Zeit. angew. Chem.* 1904, 1398.

A further reaction also takes place, according to Trautz,[1] to a subordinate extent in the chambers, namely, the formation of nitrosodisulphonic acid, $NO(SO_3H)_2$, by the action of nitrous acid on sulphurous acid, which then, with excess of nitrous acid, yields sulphuric acid and nitric oxide,

$$NO(SO_3H)_2 + 2HO.NO = 3NO + 2H_2SO_4.$$

It seems probable that in practice all these reactions as well as others not yet recognised may occur to some extent simultaneously or at different stages of the process, but that the bulk of the acid is produced in the manner indicated by the theories of Berzelius and Lunge.

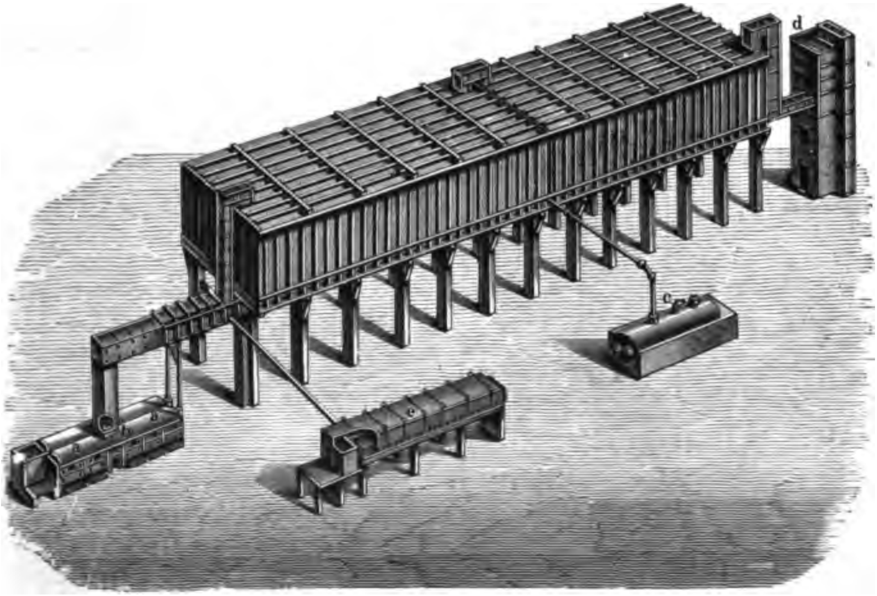

FIG. 110.

According to all these theories, the nitrous fumes act as a carrier between the oxygen of the air and the sulphur dioxide, so that, theoretically, a small quantity of these fumes will suffice to cause the combination of an infinitely large quantity of sulphur dioxide, oxygen, and water to form sulphuric acid.

Practically, however, this is not the case, because, instead of

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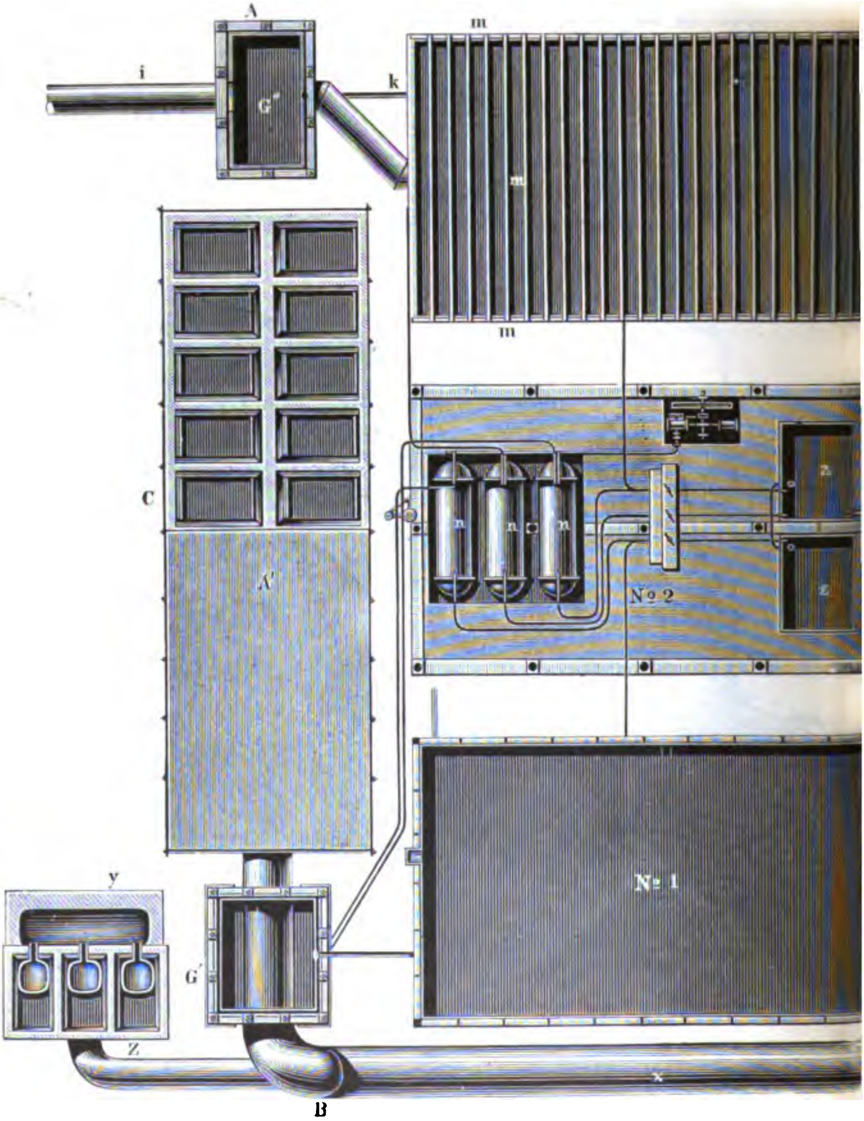
[1] *Zeit. physikal. Chem.* 1904, **47**, 600.

pure oxygen, air must be used, and four-fifths of this consists of nitrogen, which so dilutes the other gases that in order to obtain the necessary action a considerable quantity of these oxides of nitrogen must be added. Besides this, nitrogen



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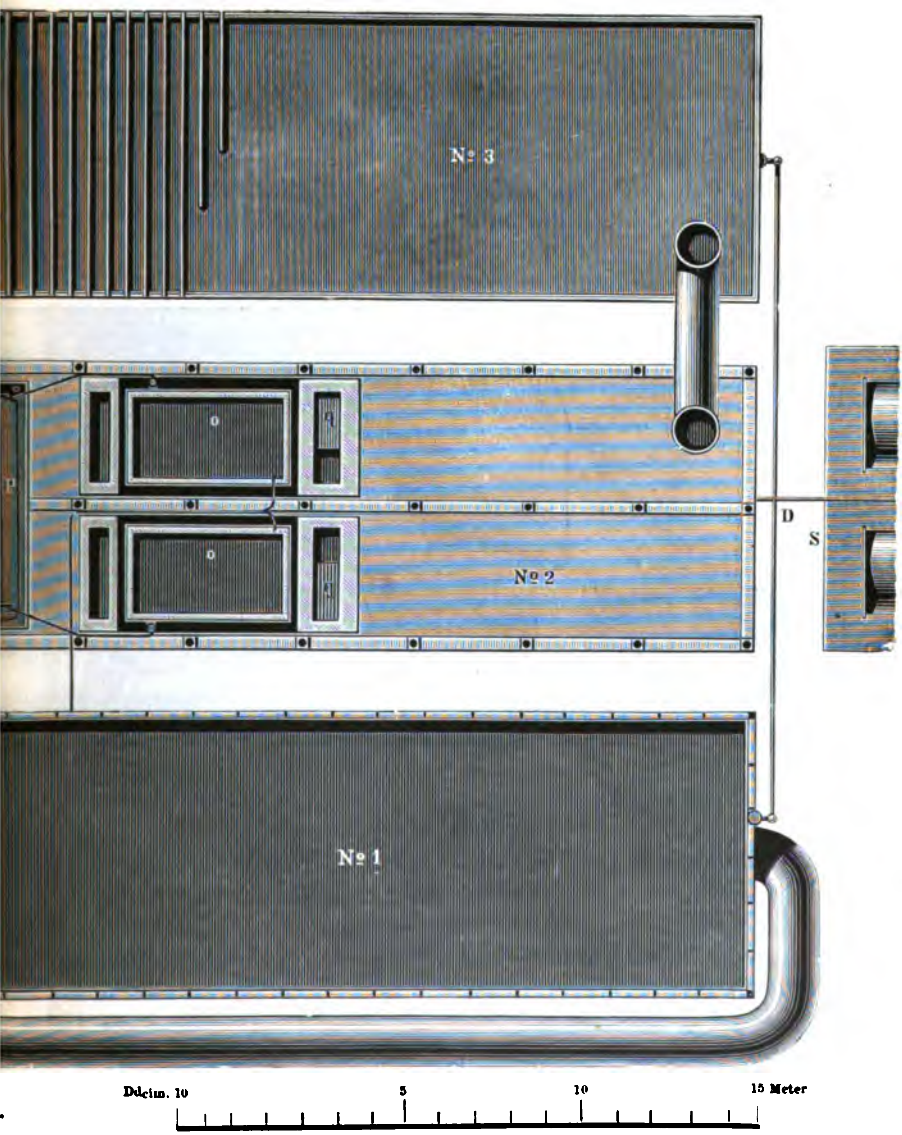
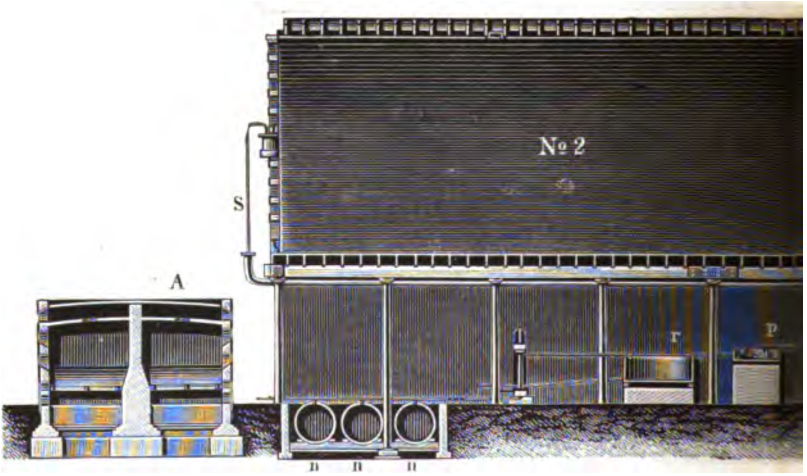
has to be constantly removed from the chambers, and in its passage carries much of the nitrous fume away with it, although most of this can, as we shall see, be recovered and used over again.



The above reaction can be illustrated on the small scale by the apparatus shown in Fig. 109, in which sulphur contained in the bulb-tube is allowed to burn in a stream of air, supplied from the double aspirator; the sulphur dioxide and air pass through the wide glass tube into the large glass globe, but carry in on their way the nitrous fumes generated in the small flask (*a*) from nitre and sulphuric acid. The flask (*b*) contains boiling water, from which steam passes into the globe. The outlet tube (*c*) of the globe communicates with a draught. By alternately increasing and diminishing the supply of sulphur dioxide, the disappearance and reappearance of the red nitrous fumes can be



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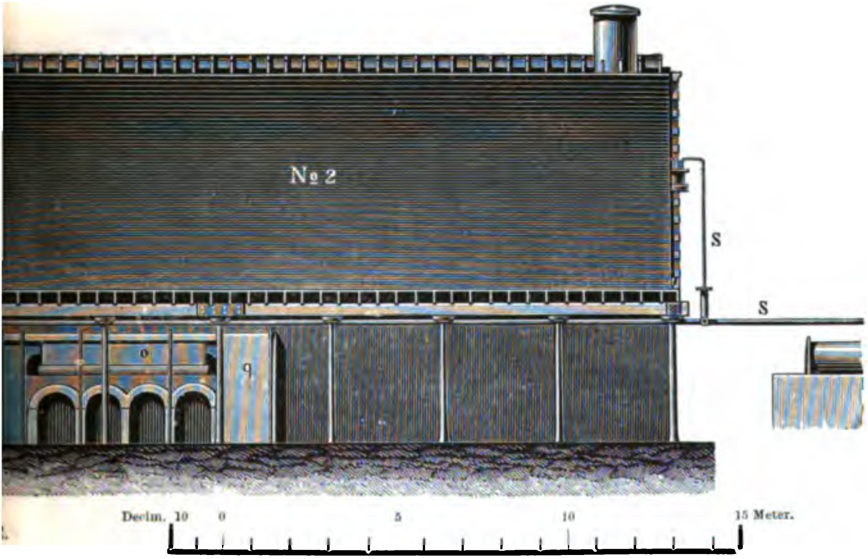
readily shown. If the flask be kept dry whilst the two gases are passed in, the white "lead-chamber crystals" are seen to be deposited on the glass. When aqueous vapour is admitted, the crystals dissolve with formation of sulphuric acid and ruddy fumes.

231 The leaden chambers for the manufacture of sulphuric acid are now constructed of a much larger size than was formerly the case, but vary considerably in different works; they are frequently 30 meters in length, 6 to 7 meters in breadth, and about 5 meters in height, and have therefore a capacity of from 900 to 1,000 cubic meters (about 38,000 cubic feet). The chambers are made of sheet lead weighing 35 kilos per square meter (or 7 lbs. to the square foot), and soldered together by melting the edges of the two adjacent sheets by means of the oxyhydrogen blow-pipe. The leaden chamber is supported by a wooden framework to which the leaden sheets are attached by strips of the same metal, and the wooden framework is generally raised from the ground on pillars of brick or iron and the whole erection protected from the weather, sometimes by a roof, but at any rate by boarding to keep off most of the rain. The space below the chamber is used either for the sulphur burners or for the concentrating pans.

The general appearance or bird's-eye view of a sulphuric acid chamber is shown in Fig. 110, whilst the arrangement and construction of a very complete form of sulphuric acid plant now in use in this country is shown in Figs. 111, 112, and 113. Three chambers, termed respectively Nos. 1, 2, and 3 (Fig. 111), are placed side by side supported on iron pillars ten feet high. Each chamber has the dimensions already given, and each, therefore, has a capacity of 38,500 cubic feet. A longitudinal section of the chamber (No. 2) in the direction (DC) is shown in Fig. 112, and a sectional elevation in the direction (AB) is shown in Fig. 113. From this last figure it is seen that the roof of the chamber is not horizontal but slightly slanting so as to enable the rain to run off into gutters placed to receive it.



232 Beginning at the first part of the process we find the pyrites-kilns, or burners placed across the ends of the chamber as seen in plan at A, Fig. 111, in longitudinal section and in elevation at A, Fig. 112, and in cross section at A, Fig. 113. The broken pyrites, FeS_2, is filled, in moderately sized lumps, into the burners, which have previously been heated to redness, and when the burning is once started the fire is kept up by placing a new charge on the top of that nearly burnt out. The ordinary charge for each burner of pyrites, containing about 48 per cent. of sulphur, is 6 to 8 cwt., which is burnt out in twenty-four hours, and the kilns are charged in regular succession, so that a constant supply of gas is evolved during the whole time, whilst the quantity of air which enters the kiln is carefully regulated by a well-fitting door placed below.

The hot sulphur dioxide, nitrogen, and oxygen gases are drawn from the pyrites burners, through the whole system of tubes, towers, and chambers, by help of the powerful draught from a large chimney which is placed in connection with the apparatus. These gases first pass from each kiln into a central flue, built in the middle of the kiln, and thence into an upright brick shaft through a horizontal earthenware flue, or cast-iron pipe, into the lower part of the square denitrating tower seen in section at G in Fig. 113. This tower, from *a* to *b*, is about 45 feet, or 14 meters, in height; it is built up, from *a* to *c*, to a height of 25 feet, or 8 meters, of lead lined with fire brick, and of this about 15 feet, or 5 meters, from *d* to *e*, are filled up with pieces of flint.

The object of this Glover's tower, or denitrating tower as it is termed, is to impregnate the sulphur dioxide as it comes from the burners with nitrous fumes derived from a later stage of the operation. This is effected by allowing strong nitrated acid to flow down the tower together with a stream of chamber-acid. Strong sulphuric acid, as we shall see, has the power of absorbing nitrous fumes, with formation of nitrosyl-sulphuric acid, $SO_2(OH)(O.NO)$, and this decomposes with evolution of nitric oxide when the acid comes into contact with the hot sulphur dioxide from the kilns:—

$$2SO_2(OH)(O.NO) + SO_2 + 2H_2O = 3SO_2(OH)_2 + 2NO.$$

Two reservoirs are placed at the top of the Glover tower; one containing the strong nitrated acid, the other containing the chamber-acid. Both the strong nitrated and the chamber-acid are allowed to flow down together over the column of flint stones

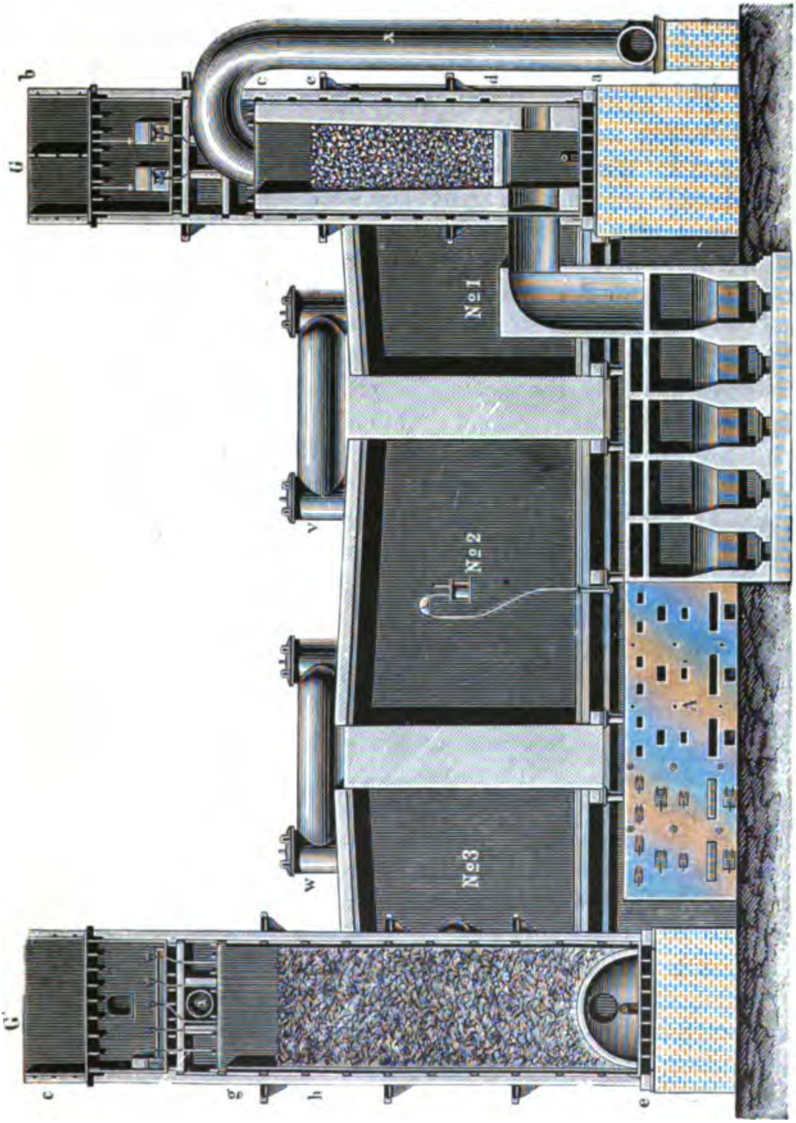


FIG. 113.

in given proportions, and when the mixture comes into contact with the upward current of hot sulphur dioxide, the nitrous fumes dissolved in the strong acid are given off and swept away, together with the gases from the burners, direct into the chambers. Although the nitrated acid loses its nitrous fumes when diluted with water, it does not do so in presence of chamber-acid of the ordinary strength, so that the denitrating effect of the Glover's tower depends on the reducing action of the sulphur dioxide, rather than on any dilution by the chamber-acid. This addition is mainly made for the purpose of cheaply concentrating the chamber-acid, for not only does the strong acid lose its dissolved nitrous fumes, with the production of a considerable amount of acid, but the weak chamber-acid coming in contact with the hot dry gases which enter the tower at a temperature of 340°, parts with a large quantity of its water, which goes into the chamber as steam, whilst the concentrated acid, falling to the bottom of the tower, flows into a reservoir, z, Fig. 111, placed to receive it.

On issuing from the tower, the gas, having now been cooled by contact with the stream of acid to a temperature of about 60°, passes into the cast-iron pipe, *x*, Fig. 113 (4 feet 6 inches in diameter), whence it is delivered at the further end of chamber No. 1 at a height of 8 to 9 feet above the floor.

233 The supply of nitrous fumes, which is needed to act as carrier of the atmospheric oxygen to the sulphur dioxide, is in this country usually furnished by the nitre pots shown in section in Fig. 114. The charges of 30 lbs., or 13·5 kilos, of sodium nitrate, and 33 lbs., or 15 kilos, of sulphuric acid, of sp. gr. 1·75, are run into the pots from the outside, and after the lapse of two hours, when each charge is exhausted, the fused sodium bisulphate (technically termed sale nixum) is run off into a pan placed on a platform outside the oven, and a new charge introduced. The decomposition of the nitre is accelerated by heat from the pyrites burners, placed below the brick arch which separates them from the pots, and the nitric fumes are gathered into a cast-iron pipe, z, Fig. 114, which discharges its contents into the long horizontal main carrying the products from the pyrites burners into the chamber. Here also the nitric acid vapour parts with some of its oxygen, and is reduced by the sulphur dioxide to the lower oxides, which act as a carrier between the oxygen and sulphur dioxide.

In place of the nitre pots, many continental works manufacture nitric acid in a separate plant (described later on under nitric acid), and allow this to flow into the Glover tower along with the nitrated strong sulphuric acid.

The mixture of oxygen, nitrogen, sulphur dioxide, nitrous fumes and vapour of water now meets with steam introduced into the chamber by the tubes, s s, Fig. 112, and the reaction as already described sets in. Having travelled through the length of chamber No. 1, the gases pass by means of the connecting shaft (v) shown in Fig. 113, into the second chamber, where they likewise meet with steam jets or finely divided water spray, and having passed through this chamber, and deposited a further amount of liquid sulphuric acid, which falls on the floor of the chamber, the gases are drawn into the third or exhaust chamber by the flue (w) shown in Fig. 113. Here, if the process is properly worked, all the sulphur dioxide is converted into sulphuric acid, and red nitrous fumes must always be visible. For the purpose of determining the proper working of the process the percentage of sulphur dioxide contained in the gases entering the first chamber, and that of the oxygen in the gases leaving the third chamber, is regularly ascertained in carefully managed works.

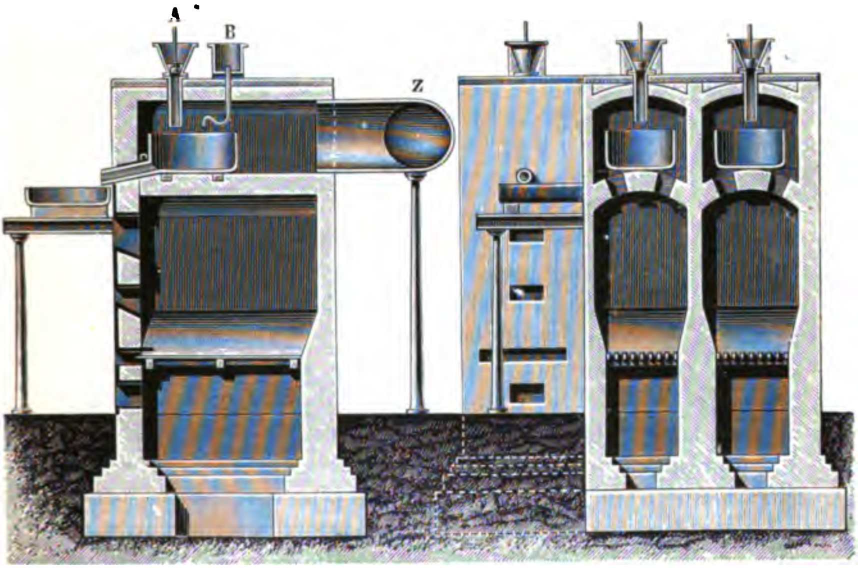


Fig. 114.

The formation of the sulphuric acid takes place most rapidly in the inlet portion of the first chamber, and becomes slower as the reacting gases become more dilute. In recent years special towers devised by Lunge have been employed in a number of works either in place of, or in addition to, the subsequent chambers. These towers consist of a leaden shell, filled with a series of specially constructed stoneware plates, pierced with holes, the plates being so arranged that the holes in each are opposite the non-perforated portion of the one above. In passing through the tower, the gases are thoroughly mixed and brought into intimate contact with the mist of dilute sulphuric acid mechanically carried along with them, which greatly accelerates the production of acid. As, however, the reaction takes place more rapidly and in a smaller space than is the case when leaden chambers are used, the heat evolved would raise the temperature above that best suited to the process, and to overcome this difficulty dilute sulphuric acid is continuously pumped through the tower, the excess of heat being then absorbed by evaporating the water; the water vapour formed mixes with the gases, thus effecting a saving in the quantity of steam or water spray which has to be introduced, and at the same time concentrating the acid. The introduction of these towers has in many cases largely increased the productive capacity of the plant, and in some has also effected considerable saving in the quantity of nitre used.

Another recent modification is the system of tangential chambers patented by T. Meyer.[1] In this system the chambers are circular or polygonal in horizontal section, a number of these being arranged in series; the gases enter the side of the first chamber at a tangent, and leave by a pipe through the centre of the bottom, passing thence to the second chamber, which is also entered at a tangent, and so on through the series. By this means the gases are compelled to take a spiral course through each chamber, which is stated to effect a better mixing, resulting in a larger output of sulphuric acid per unit of chamber space.

234 The nitrous fumes having been added in excess of the quantity required to convert the SO_2 into H_2SO_4 still remain in chamber No. 3, and, in order to absorb these, a Gay-Lussac tower (G″, Figs. 111 and 113) is employed, the capacity of which ought to be at least one-hundredth part of that of all the chambers. This consists, like the Glover tower, of a square tower 50 feet in height, made of strong lead (7—8 lb.) and lined for 35 feet with 2 inch thick glazed fire tiles, and filled with coke. A

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[1] *Zeit. angew. Chem.* 1899, 159, 655.

Lunge "plate-tower" may also be employed in place of the Gay-Lussac tower. The exit gases from chamber No. 3 are drawn in at the bottom of this coke column, and escape to the chimney by the exit tube (*i*, Fig. 113) at the top. In their passage they come in contact with a finely divided shower of strong cold acid (sp. gr. 1·75) obtained by concentrating the chamber-acid. This strong sulphuric acid absorbs the excess of nitrous fumes which would otherwise pass away up the chimney, and having thus become saturated with nitrous fumes, runs away through the spout *k* into reservoirs for the so-called nitrated acid, built under chamber No. 3, the position of which (*mm*, Fig. 111) is shown on the plan. From these reservoirs the nitrated acid is allowed to run into one of the cast-iron air boilers (*nnn*) shown on the plan, whence, by air pressure, it is forced up to the cistern on the top of the Glover tower for employment in the first part of the process as already described.

235 The continuous process of acid-making in the chambers is only carried on until the acid has attained a specific gravity of 1·53 to 1·62, or contains 62–70 per cent. of the pure acid, H_2SO_4, inasmuch as an acid stronger than this begins to absorb the nitrous fumes. In order to obtain a stronger acid, either the arrangement of the Glover tower, as described, is employed or, in works where the Glover is not used, the chamber-acid is run into the leaden concentrating pans (*oo*) placed under chamber No. 2, shown in plan in Fig. 111, and in section in Fig. 112. The flame and heated air from the fires (*q*) play over the surface of the acid contained in these pans, the water passes away in the form of steam, and the strong acid remains. By this means the acid can be concentrated until it attains a specific gravity of 1·72, or contains 79 per cent. of pure acid; beyond this degree of concentration the hot acid begins rapidly to attack the lead of the pans, and it therefore cannot be further evaporated in them. It is then run off into the acid cooler (*p*), a leaden trough surrounded by cold water, whence it passes into the strong-acid cisterns (*r*, Fig. 112). In this form the acid is technically known as B. O. V., brown oil of vitriol, as it is always slightly coloured from the presence of traces of organic matter, and it is in this condition that it is very largely sold for a great variety of purposes.

236 In order to drive off the remaining portions of water the acid must be concentrated in platinum or glass vessels. A recent form of platinum still, designed by Delplace and

manufactured by Messrs. Johnson, Matthey and Co., of London, is shown in Figs. 115, 116. Two of these stills, AA, BB, are worked together in series, the dilute acid being partially concentrated in AA and passing thence by means of a platinum tube to BB, in which the concentration is completed. The strong acid is cooled by passing through a platinum cooler, C (Fig. 116), which is immersed in a leaden vessel into which cold water is constantly running.

Each of the stills shown in the figure is capable of producing 10 tons of 94 per cent. oil of vitriol per 24 hours under ordinary working conditions, or about one-half of that quantity of 97·5 per cent. acid.

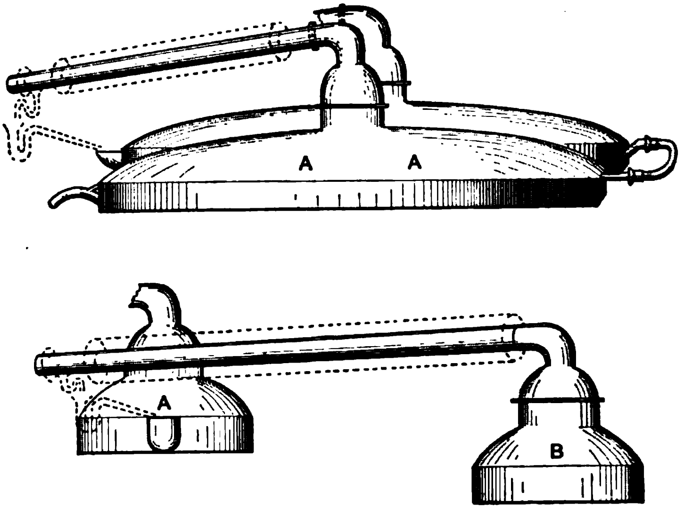

Fig. 115.

In many English works the sulphuric acid is rectified in glass and not in platinum vessels. These glass vessels are large retorts made of well-annealed and evenly-blown glass (*a*, Fig. 117), of such a size as to contain twenty gallons of the acid. Each retort is placed on an iron sand-bath (*b*), round which the flames from a fire are allowed to play, but so that the flame does not touch the retort. A glass head (*c*) fits loosely into the neck of the retort, and through this the aqueous vapour, carrying with it a little acid fume, passes into a condensing box. The plan of a rectifying house containing twenty-four retorts is shown in Fig. 118. The acid having been concentrated in the leaden pans (AAA), passes along the leaden tubes (BBB), from which the retorts are filled by means of the upright leaden tubes (*d*, Fig. 117), which can be bent so as to discharge the acid into the neck of the retort. After the rectification is complete the retorts are allowed to cool for twelve hours, and the acid is then drawn out by means of leaden syphons into the stoneware coolers (*i*, Fig. 117).

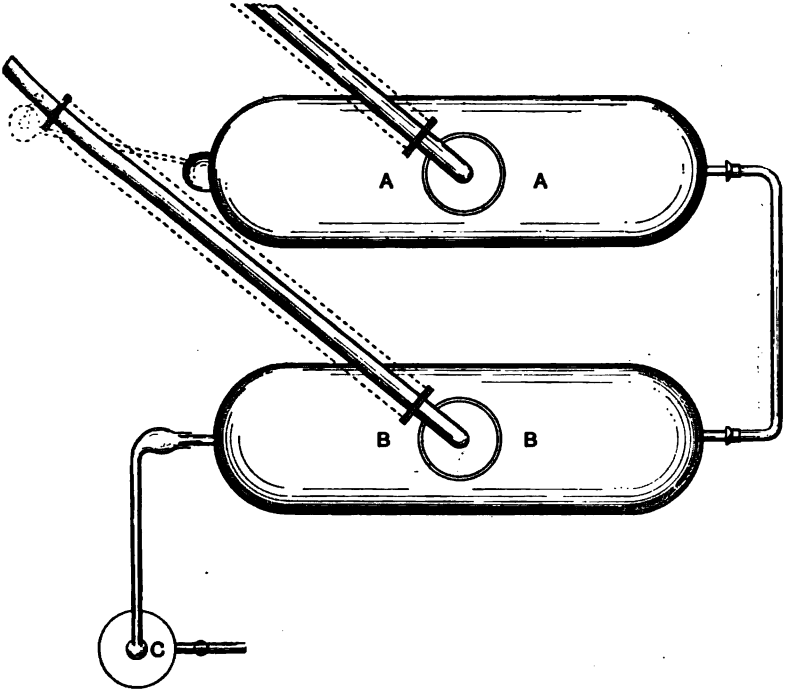

FIG. 116.

In order to effect a continuous rectification in glass vessels the following arrangement has been adopted in some works. Three of the retorts are placed one above the other, as is shown in Fig. 119. As soon as the acid in retort (B) has attained a specific gravity of 1·84, the retort is connected with a system of syphon tubes (*fff*), and acid of the specific gravity of 1·74, and having a temperature of 150°, is allowed to run into the uppermost retort (D) by means of the stopcock. This acid gradually passes through the three retorts, D, C, and B, and when it has reached the last one it has attained a specific gravity of 1·84, and is allowed to run off through a cooling chamber (*h*) into the carboy. Another efficient system of continuous concentration in glass vessels has been patented by Webb,[1] and improved by Levinstein,[2] by means of which acid containing about 96 per cent. of H_2SO_4 (sp. gr. 1·84) can be obtained in a single operation from acid of sp. gr. 1·625, containing about 71 per cent. of H_2SO_4.

237 According to theory, 100 parts of sulphur should yield 306·25 parts of pure sulphuric acid. In practice, however, this theoretical yield is never attained, and for several reasons; in the first place because a certain amount of loss must necessarily take place in working with such enormous volumes of gas, and in the second place inasmuch as an unavoidable loss occurs in the processes of concentration; and thirdly, owing to the fact that an amount of sulphur varying from 2 to 5 per cent. remains behind in the burnt ore, and this amount cannot be accurately allowed for. As a general rule a yield of 270 to 280 parts of pure acid from 100 of sulphur is practically considered about the proper production, so that about 5 per cent. of sulphur is lost on the average, of which, however, only a portion passes out in the gaseous form into the air. In cases where special precautions are taken the yield sometimes reaches from 294 to 297, but when the manufacture is not carefully conducted much more serious losses occur. Thus in his eighth annual report

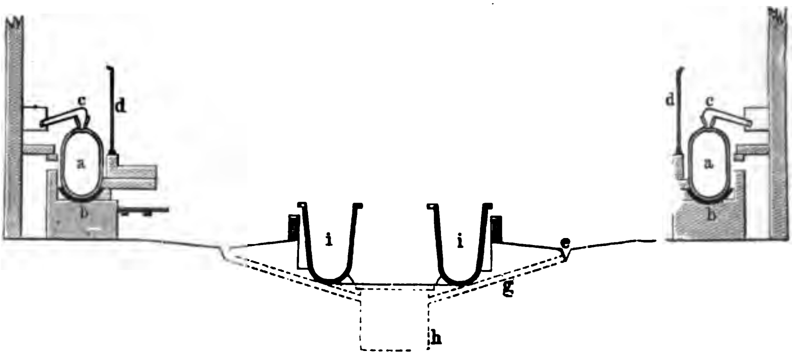

Fig. 117.

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[1] Eng. patent, 2,343, 17,407, and 18,891 (1891)
[2] *Ibid.* 19,213 (1892).

(1871, p. 17) Dr. R. Angus Smith gives a table, showing the total escape of sulphur acids (calculated as sulphuric acid) from twenty-three chemical works. From this it appears that whilst from some of the works no escape of these acids occurs, the average loss of sulphuric acid in the twenty-three works in question is 7·606 per cent. on the total quantity obtainable from the sulphur burnt, and that the loss in the case of four works actually rises to more than 20 per cent., in one case amounting to an escape of 159 lbs. of sulphuric acid every hour. Facts like these, says the inspector, dispose of the argument often used by the manufacturers, that they require the acid, and that it is to their interest to keep it, and of course condense it to the best of their power. Indeed, certain makers are fully aware that they are allowing sulphuric acid to escape in large quantities, but their reply is that it is cheaper to permit a large escape and work rapidly rather than have large chambers and condense the whole of their gases.

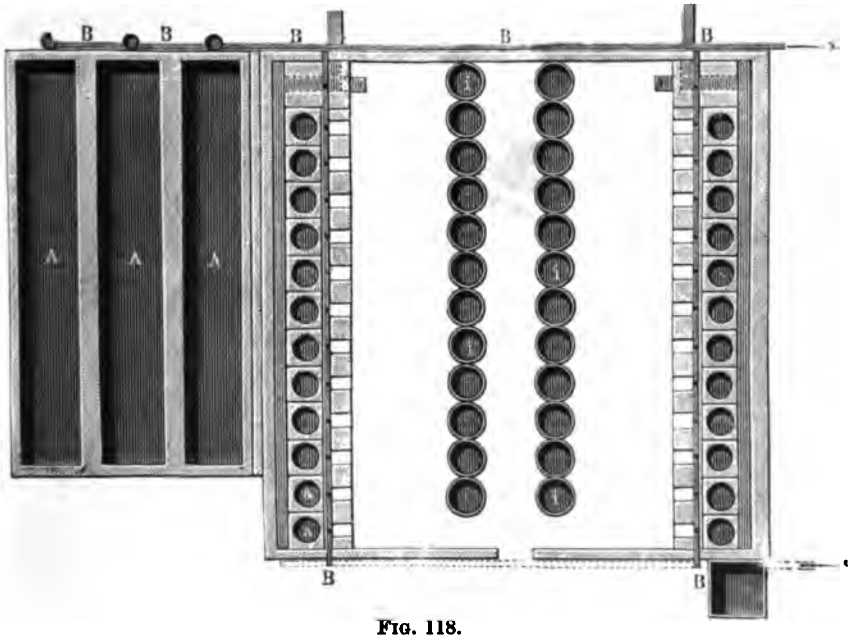

FIG. 118.

By the Alkali Act of 1881 the limit of 4 grains per cubic foot has been set to the amount of sulphuric anhydride which may be left in the gases escaping from the chambers. The amount actually escaping during the year 1903 was found by the Inspectors under the Alkali Act to average 1·248 grains.[1]

The amount, again, of sodium nitrate or Chili-saltpetre used, varies considerably even in the best works, according to the rate at which the reaction is permitted to proceed, and the completeness and rapidity with which the nitrous fumes can be recovered in the Gay-Lussac tower and again brought into the chamber. Manufacturers who employ Glover and Gay-Lussac towers use on an average 3·5 to 6·5 parts of nitrate for every 100 of sulphur burnt, whilst at works where these appliances are not in use the quantity of nitre required may rise to from 12 to 13 parts. The larger the quantity of nitrous fumes present in the chamber, the quicker will be the formation of sulphuric acid, and the proportion of fumes which pays best is a question for the manufacturer in each instance to decide. A certain loss of oxides of nitrogen cannot, of course, be avoided; the fumes are partly not completely condensed, and pass out by the chimney, and partly, in all probability, reduced by the sulphur dioxide to nitrous oxide or even to nitrogen, which, as they cannot combine again with the

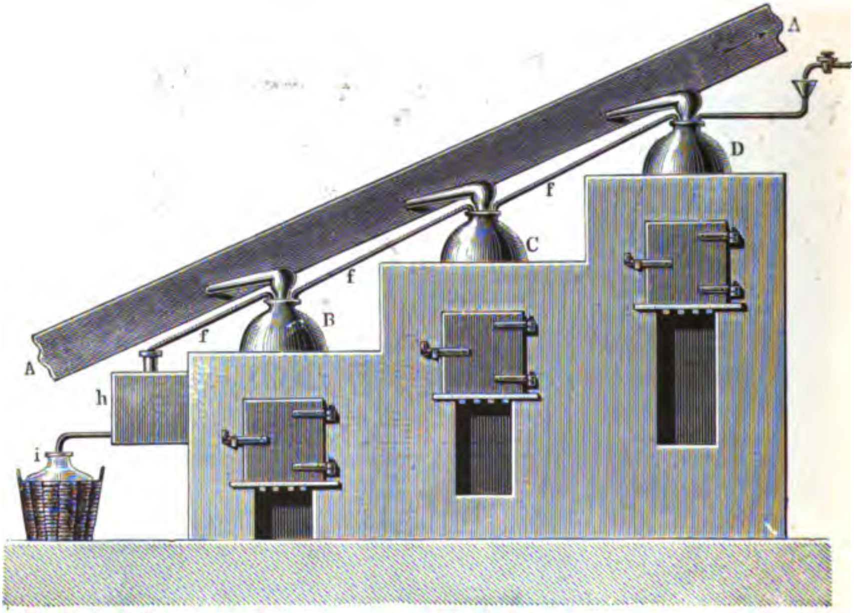

FIG. 119.

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[1] *Report of Chief Inspector of Alkali Works*, 1903, p. 8.

atmospheric oxygen, must escape into the air. The loss due to formation of nitrous oxide and nitrogen is, however, very slight.[1]

In order to convert 100 parts of sulphur into sulphuric acid in the lead chambers, about 210 parts of water in the form of steam are required in actual practice. This steam is costly in its production, and in many cases the necessary water is now more economically introduced in the form of a very finely divided spray or mist, according to the suggestion first made by Sprengel in 1873.

MANUFACTURE OF SULPHUR TRIOXIDE, SULPHURIC ACID, AND FUMING SULPHURIC ACID BY THE CONTACT PROCESS.

238 As already mentioned (p. 403) the first successful processes for the large scale production of sulphur trioxide by the combination of sulphur dioxide and oxygen in presence of a solid catalytic agent were brought out simultaneously in 1875 by Squire and Messel in England and by Winkler in Germany. In both processes a mixture of sulphur dioxide with oxygen in the exact proportions required was obtained by decomposing at a high temperature sulphuric acid (previously obtained by the chamber process), when it is resolved as follows:

$$2H_2SO_4 = 2SO_2 + O_2 + 2H_2O.$$

The steam was removed by passing the resulting gases through concentrated sulphuric acid, and the dried mixture then passed over heated spongy platinum or platinised asbestos, the trioxide produced being absorbed in sulphuric acid and yielding the fuming acid. Such a process could not, of course, form a commercial method of preparing ordinary sulphuric acid, inasmuch as this acid itself formed the starting point, but it permitted of the production of the fuming acid at a price allowing competition with that produced by the Nordhausen process (p. 427). The wear and tear of the plant for the decomposition of the sulphuric acid was, however, very great, and many attempts were made to produce a suitable mixture of the dioxide and oxygen by more economical processes. Thus, in 1887 Schröder and Haenisch patented one in which the

[1] Inglis, *J. Soc. Chem. Ind.* 1904, 643.

sulphur dioxide given off in the roasting of sulphur ores such as zinc blende was absorbed by water, the gas again driven off from the solution by heat, dried, and, after mixing with the requisite quantity of air, passed over platinum.

At this time it was generally supposed that to obtain anything like a quantitative production of the trioxide, an essential condition was the presence of the sulphur dioxide and oxygen in the exact proportion of two volumes of the former to one of the latter, and it was only after the publication of the patents of the Badische Anilin- & Soda-Fabrik in 1898 that the fallacy of this view was generally recognised, and the fact became known that an excess of oxygen is necessary for the complete conversion of sulphur dioxide into the trioxide. Winkler had made the same observation as early as 1878, but his results were not published until quite recently.

The recognition of this fact paved the way for the direct production of the trioxide from the pyrites burner gases, containing about 7 per cent. of sulphur dioxide, 10 per cent. of oxygen, and 83 per cent. of nitrogen. Very many difficulties both of a chemical and mechanical nature had to be overcome before the technical success of the process was assured, and the manner in which these difficulties were systematically investigated and finally surmounted is fully described in a lecture[1] given before the Berlin Chemical Society in 1901 by Dr. Knietsch of the Badische Anilin- & Soda-Fabrik.

The greatest initial difficulty lay in the fact that the catalytic action of the platinum used as contact substance rapidly diminished when the process was conducted on the large scale. It was found that to maintain the metal in an active condition, all particles of dust, as well as the mist of finely divided sulphur particles and of sulphuric acid always present in the burner gases, must be absolutely removed; moreover, that every trace of arsenic must be eliminated, as the minutest quantity of this element rapidly paralyses the catalytic action of the platinum, acting in the same manner as poison on a living organism (p. 333). To effect this purification, the burner gases, in the process as described, are treated with a jet of steam in the dust flue, and gradually cooled by passing through a series of leaden pipes until the temperature is reduced to 100°. They then pass through leaden scrubbers containing water, which is thereby converted into dilute sulphuric acid, and the gases are

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[1] *Ber.* 1901, **34**, 4069.

finally dried by concentrated sulphuric acid. Before passing to the contact apparatus, the gases are tested for freedom from suspended particles by examining a layer some yards in length illuminated at the further end by a beam of light, and are also chemically tested to ascertain the absence of arsenic.

In order to start the combination of sulphur dioxide and oxygen in presence of platinum the gases must be heated to a temperature of about 300°, but when the reaction commences a large quantity of heat is evolved, the thermochemical change being represented by the equation:—

$$SO_2 + O = SO_3 + 22{,}600 \text{ cal.}$$

On the small scale this heat is so rapidly radiated that the temperature does not rise very high, but on the large scale the radiation is proportionally much less, and unless special means of dissipating the heat of the reaction are employed, the temperature rises to such an extent that dissociation of the trioxide occurs. The tubes containing the contact substance are therefore cooled either by allowing a regulated current of air to circulate round them, or by passing the purified and cooled burner gases over them before entering. A form of contact furnace in which the latter method is used is shown in Fig. 120. Within the brickwork, *MM*, is fixed the iron cylinder, *SS*, with top and bottom covers, *WW'*, and tubes, *RR*, passing through the diaphragm, *DD'*. The whole can be heated by a fire lighted at *hh'*, the waste gases escaping at *L*. The purified burner gases pass first through the heat regulator into the chambers, *AA'*, and are distributed uniformly around the outside of the tubes, *RR*, through the pipes, *O F*, to the chamber, *N*, and thence, after being mixed by the baffle plates in the latter, pass through the tubes, *RR*, containing platinised asbestos. The latter is packed between perforated plates dropped on to an iron rod fixed in the centre of the tube, and kept at suitable distances by pieces of iron tube of the requisite length, placed on the rod above each plate. In this manner an intimate contact of the gases with the platinised asbestos is ensured without causing a large back pressure.

In starting the apparatus a fire is kindled at *hh'* until the temperature at *D* is found to be about 300°. The burner gases are then allowed to enter at *A*, and the formation of sulphur trioxide proceeds without the aid of extraneous heat, whilst the temperature is prevented from rising too high by the transference of the heat of combination to the entering gases. The temperatures in *D* and *D'* are regulated by manipulating the valves *V*, *V'*, and *V''*, if necessary with the aid of the heater *G*, and the inlet and outlet gases tested until a maximum conversion of the dioxide into the trioxide is obtained. With proper working 96–98 per cent. of the sulphur dioxide is converted into trioxide, and each tube produces 40–50 kilos of the latter per 24 hours.

The sulphur trioxide produced may be then condensed and stored in drums of tinned iron, but is mostly converted at once into concentrated or fuming sulphuric acid. Trouble was at first experienced in effecting a complete absorption of the trioxide, owing to the formation of a white mist of sulphuric acid, which could only be retained with great difficulty. It was found, however, that the absorption is complete and almost instantaneous if 97–98 per cent. sulphuric acid is used as absorbent. The gases after leaving the kiln are therefore passed through cast-iron absorbing vessels containing acid of

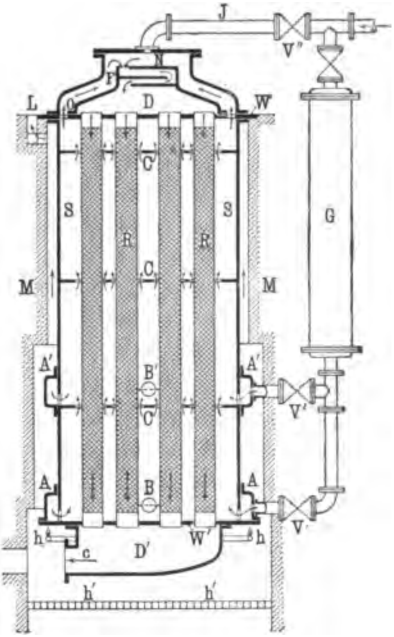

FIG. 120.

this strength, a stream of water or dilute sulphuric acid being simultaneously run in at such a rate as to maintain the acid at that concentration. If fuming sulphuric acid is required one or more absorbers containing concentrated sulphuric acid are placed in front of the first, these being made of wrought iron, which is not attacked by acid of this strength, whereas cast iron, although not corroded, rapidly cracks under these conditions.

The illustration in Fig. 121 represents diagrammatically the whole process. The sulphur dioxide evolved from *A*, after passing through the drying apparatus, *B*, mixes at *C* with air forced in by the pump, *D*. The mixed gases enter the washer, *E*, containing a hood with serrated edges, which forces the gas in fine streams through sulphuric acid of sp. gr. 1·84, and thence through the "stripper," *F*, which is similar to *E*, but contains no liquid except such as is deposited from the gas, and serves to remove mechanically carried liquid particles. The gas then passes through the "contact" furnace, *H*, to the fuming acid absorber, *I*, immersed in a cooling vessel, having a suspended wrought-iron hood with serrated edges and filled with sulphuric acid of sp. gr. 1·84, which absorbs the trioxide with formation of the fuming acid. The unabsorbed trioxide passes to the second absorber, *J*, of cast iron, which serves to absorb the remainder in 97–98 per cent. acid as already described.

239 A number of other "contact" processes are now in use in addition to the Ludwigshafen process. Messrs. Meister, Lucius, and Brüning at their Höchst works employ ferric oxide as the contact substance, but in this case only 60–66 per cent. of the sulphur dioxide is converted into the trioxide, and the exit gases must then be further treated with platinum or conveyed to ordinary sulphuric acid chambers. Such details as are known of the remaining processes may be found in the 1903 edition of Lunge's volume on *Sulphuric Acid*.

The manufacture of fuming sulphuric acid from green vitriol, by which both fuming and ordinary acid were first produced, has now been entirely abandoned, as the fuming acid can be prepared more cheaply by the "contact" processes. This method was originally carried out in the Nordhausen district, from which the name Nordhausen acid is frequently given to the fuming acid. Latterly, the process was carried out solely at the works of J. D. Starck in Bohemia. A solution of green vitriol was obtained by the oxidation of iron pyrites, evaporated down and roasted in the air, being thus oxidised to a basic ferric

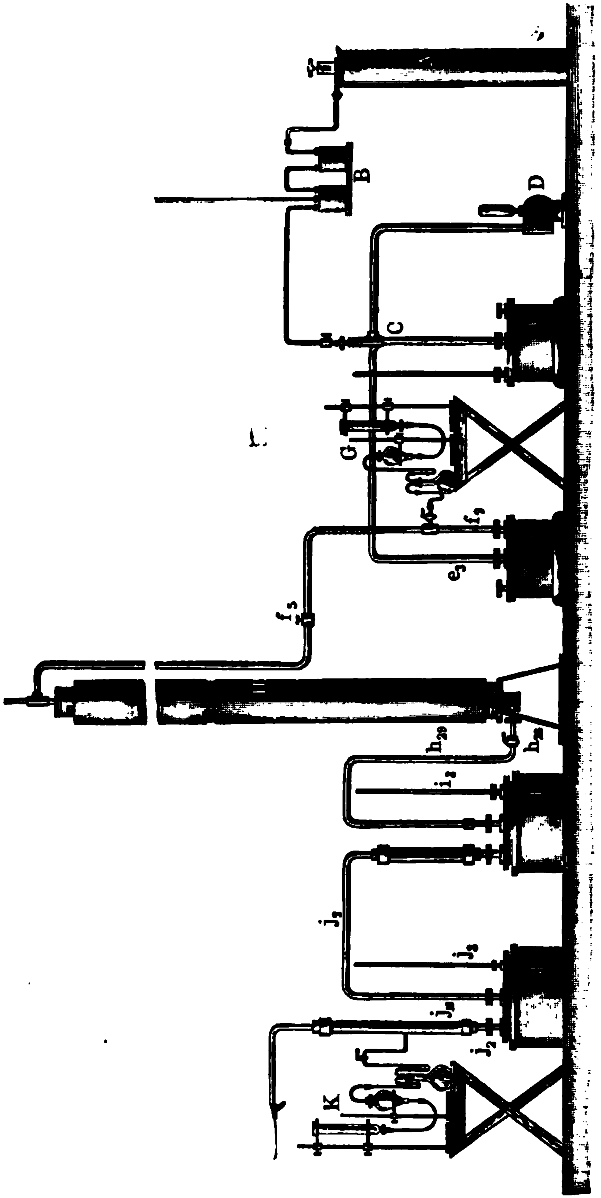

FIG. 121.

sulphate, $Fe_2S_2O_9$. On heating the latter in clay retorts, the following decomposition took place:

$$Fe_2S_2O_9 = 2SO_3 + Fe_2O_3.$$

Part of the trioxide combined with the water still present to form sulphuric acid, the latter dissolving the remainder with formation of the fuming acid.

240 None of these processes yield, it must be remembered, chemically pure acid, inasmuch as, in the first place, the water cannot thus be completely removed, and secondly, because, in the chamber process especially, impurities such as sulphate of lead, arising from the action of the acid on the leaden concentrating pans, and arsenic derived from the pyrites, are not got rid of by this process of simple concentration.

In order to prepare pure sulphuric acid, the commercial product must be distilled in a glass retort until one-third has passed over; then the receiver is changed and the acid distilled nearly to dryness. It not unfrequently happens that in this process the acid bumps violently on ebullition, owing to a small quantity of solid lead sulphate being deposited on the bottom of the retort; the addition of small pieces of platinum foil or wire stops this to a certain extent, but a better preventive is either to heat the retort at the sides rather than at the bottom, or, when the ebullition becomes percussive, to allow the liquid to cool, then to pour off the clear acid, leaving the deposit behind, and to proceed with the distillation of the clarified liquid. A slow current of air passed through the boiling acid has also been found efficacious.

241 *Properties.*—The acid thus purified by distillation still contains about 1·5 per cent. of water which cannot be removed by this process. If, however, the distillate be cooled, the pure acid containing 100 per cent. of H_2SO_4 separates out in the form of crystals which melt at 10·5°. These crystals when once melted generally remain liquid for a considerable time, even when cooled below their freezing point, the liquid only solidifying when it is agitated or when a small crystal of the acid is added, the temperature then rising to 10·5°. The specific gravity of the pure liquid acid is 1·837 at 15° compared with water at 4° (or, as it is usually expressed, 15°/4°),[1] whilst according to Lunge and

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[1] Marignac, *Ann. Chim. Phys.* 1853, [3], 39, 184; Mendelejeff, *Ber.* 1884, 17, 2536.

Naef[1] it is 1·8384. When the pure acid is heated, it begins to fume at 30°, inasmuch as it then partially decomposes into water and sulphur trioxide. This dissociation increases with increase of temperature until at 338°, the boiling-point of the liquid (Marignac), a large quantity of trioxide is volatilised, so that the residue contains from 98·4 to 98·8 per cent. of the real acid, and then this liquid may be distilled without alteration. The vapour of sulphuric acid when it is more strongly heated completely decomposes into water and the trioxide.

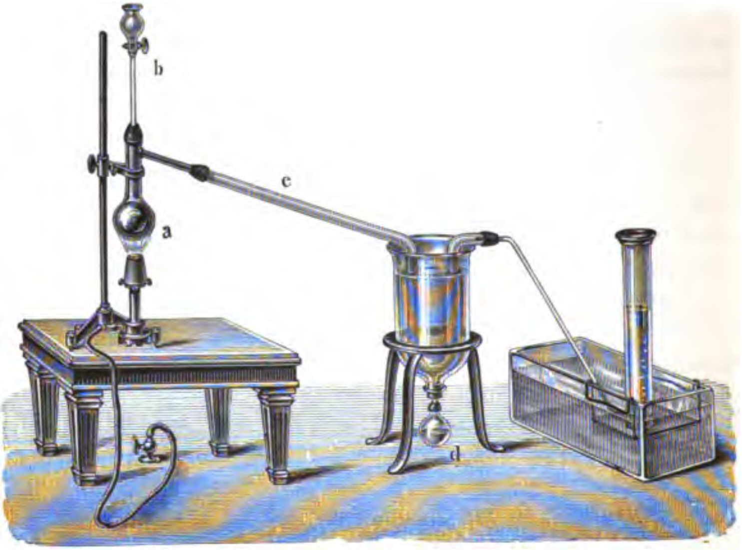

Fig. 122.

According to Deville and Troost the vapour density at 440° is 25, whilst for equal volumes of aqueous vapour and sulphur trioxide the calculated vapour density is

$$\frac{17·88 + 79·46}{4} = 24·36.$$

When heated still more strongly, the trioxide thus formed itself splits up into oxygen and sulphur dioxide. This decomposition may be readily shown by allowing sulphuric acid to drop slowly into the platinum flask (*a*, Fig. 122), which is filled with pumice-

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[1] *Chem. Industrie*, 1883, 37.

stone and heated strongly by the lamp; the mixture of gases which escapes consists of one volume of oxygen to two volumes of sulphur dioxide, which latter gas is absorbed by being passed through water containing caustic soda, the oxygen escaping in the free state, whilst any undecomposed sulphuric acid is condensed in the U-tube and collects in the flask (*d*).

242 When sulphuric acid is mixed with water a considerable evolution of heat takes place and a contraction ensues. The amount of heat which is evolved by mixing sulphuric acid and water has been exactly determined by Thomsen;[1] his results are given in the following table, in which the columns marked I. give the number of molecules of water, and II. the heat evolved in calories:—

I. x	II. $H_2SO_4 + x H_2O$.	I. x	II. $H_2SO_4 + x H_2O$.
1	6,336	49·3	16,572
2	9,355	99·7	16,744
3	11,294	200·4	16,950
5	13,020	401·7	17,196
9·1	14,851	804·4	17,522
19·1	16,147	16,09·7	17,737

From the above numbers it is seen that the addition of the first molecule produces an amount of heat represented by 6,336 thermal units, or about one-third of the total, whilst on the addition of two molecules of water about one-half the total quantity is given off. The heat evolved by a further addition of water is less for each successive molecule of water, but it has been found impossible to determine the point at which no further evolution of heat is caused by further dilution.

Hydrates of Sulphuric Acid.—When a mixture of equal molecules of acid and water is cooled down, the mixture solidifies to a mass of prismatic crystals, which possess the composition $H_2SO_4 + H_2O$, and melt, according to Pierre and Puchot, at 7°·5.

Another hydrate, of the formula $H_2SO_4 + 4H_2O$, has been isolated by Pickering[2] from a solution of sulphuric acid in water. It forms large, well-defined crystals and melts at $-25°$. This substance is characterised as a definite chemical compound by the facts that it melts and freezes at a definite temperature, and that its freezing point is lowered by the addition of either

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[1] *Therm. Unter.* **3**, 34.

[2] *Journ. Chem. Soc.* 1890, 1339.

of its components. The existence of many other hydrates of the acid has been surmised from the properties of its solution in water, but no others have as yet been isolated.

243 Sulphuric acid is largely used in the laboratory not only for the preparation of most of the other acids, but also, in consequence of its powerful hygroscopic properties, for the purpose of drying gases. To effect this, the gas is best led through tubes filled with fragments of pumice-stone which have been boiled in strong sulphuric acid. The acid is also employed to dry solid bodies, or to concentrate liquids, especially in cases where the application of a high temperature is likely to produce a decomposition of the substance, the bodies to be dried being placed over a vessel containing the acid in a closed air-space or in a vacuum.

Sulphuric acid when concentrated does not act in the cold upon many of the metals, although it does so in some cases when heated. Thus copper, mercury, antimony, bismuth, tin, lead, and silver are attacked by the hot acid, with evolution of sulphur dioxide, but are not acted on by the cold dilute acid; thus:—

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

Gold, platinum, iridium, and rhodium are unacted upon, even by boiling sulphuric acid, and this acid is, therefore, employed in the separation of silver and gold. The more easily oxidisable metals, such as zinc, iron, cobalt, and manganese, are dissolved by the dilute acid with evolution of hydrogen and formation of a sulphate, but also act upon the hot concentrated acid with production of sulphur dioxide.

Many organic bodies are decomposed by sulphuric acid, which abstracts from them the elements of water. Thus, for instance, oxalic acid, $C_2H_2O_4$, by heating with strong sulphuric acid is decomposed into carbon dioxide, CO_2, carbon monoxide, CO, and water, H_2O; and alcohol, C_2H_6O, is transformed by means of this acid into ethylene gas, C_2H_4, and water, H_2O. Wood, sugar, and other substances are blackened by strong sulphuric acid, this body withdrawing from them the hydrogen and the oxygen which they contain with production of water.

244 *The Sulphates.*—The salts of sulphuric acid are termed sulphates, and as this acid is dibasic, like sulphurous acid, two series of sulphates exist, viz., the normal salts, such as Na_2SO_4 and $CaSO_4$, and the acid salts, such as $NaHSO_4$.

Many sulphates occur native, existing as well-known and important minerals; such are:—gypsum, $CaSO_4 + 2H_2O$; heavy spar, $BaSO_4$; celestine, $SrSO_4$; Glauber's salt, $Na_2SO_4 + 10H_2O$; and Epsom salts, $MgSO_4 + 7H_2O$.

Most of the sulphates are soluble in water, and crystallise well, and these can be readily prepared by dissolving the metal in dilute sulphuric acid, or the oxide or carbonate if the metal does not readily dissolve. Some few sulphates, viz., calcium sulphate and the sulphates of lead and strontium, are only very slightly soluble, whilst barium sulphate is practically insoluble in both water and dilute acids. This fact is made use of for the detection of sulphuric acid. A soluble barium salt, usually the chloride, is added to the solution supposed to contain a sulphate; if sulphuric acid be present, a heavy white precipitate of barium sulphate, $BaSO_4$, falls down, which is insoluble in dilute hydrochloric acid. In order to detect free sulphuric acid, together with sulphates, as for instance in vinegar, which is sometimes adulterated with oil of vitriol, the liquid must be evaporated on a water-bath with a small quantity of sugar. If free sulphuric acid is present a black residue is obtained.

Free sulphuric acid is found in the water of certain volcanic districts. It has already been mentioned that sulphur dioxide occurs in volcanic gases, and these when dissolved in water gradually absorb oxygen from the air and pass into sulphuric acid. The Rio Vinagre in South America, which is fed from volcanic springs and receives its name on account of the acid taste of the water, contains free sulphuric acid. A singular occurrence of free sulphuric acid has been noticed in the salivary glands of certain mollusca; thus, according to Bödeker and Troschel, those of the *Dolium galea* contain about 2·47 per cent.

The table on the next page, prepared by Lunge, Isler and Naef,[1] exhibits the percentage of real acid, H_2SO_4, contained in aqueous sulphuric acid of varying specific gravities.

FUMING SULPHURIC ACID.

245 The manufacture of this acid has already been described together with that of sulphuric acid. It is a thick oily liquid, which is colourless when pure, but has usually a brownish colour owing to the presence of small quantities of organic

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[1] *Sulphuric Acid and Alkali*, vol. i. p. 180 (1903).

matter. It fumes on exposure to the air, owing to the evolution of sulphur trioxide, which combines with the moisture in the air to form sulphuric acid.

Degree Twaddell	Specific gravity 15°/4° *in vacuo*	Percentage of H_2SO_4	Degree Twaddell	Specific gravity 15°/4° *in vacuo*	Percentage of H_2SO_4
0	1·000	0·09	99	1·495	59·22
3	1·015	2·30	102	1·510	60·65
6	1·030	4·49	105	1·525	62·06
9	1·045	6·67	108	1·540	63·43
12	1·060	8·77	111	1·555	64·67
15	1·075	10·90	114	1·570	65·90
18	1·090	12·99	117	1·585	67·13
21	1·105	15·03	120	1·600	68·51
24	1·120	17·01	123	1·615	69·89
27	1·135	18·96	126	1·630	71·16
30	1·150	20·91	129	1·645	72·40
33	1·165	22·83	132	1·660	73·64
36	1·180	24·76	135	1·675	74·97
39	1·195	26·68	138	1·690	76·30
42	1·210	28·58	141	1·705	77·60
45	1·225	30·48	144	1·720	78·92
48	1·240	32·28	147	1·735	80·24
51	1·255	34·00	150	1·750	81·56
54	1·270	35·71	153	1·765	82·88
57	1·285	37·45	156	1·780	84·50
60	1·300	39·19	159	1·795	86·30
63	1·315	40·93	162	1·810	88·30
66	1·330	42·66	165	1·825	91·00
69	1·345	44·28	166	1·830	92·10
72	1·360	45·88	167	1·835	93·43
75	1·375	47·47	168	1·840	95·60
78	1·390	49·06		1·8410	97·00
81	1·405	50·63		1·8415	97·70
84	1·420	52·15		1·8410	98·20
87	1·435	53·59		1·8400	99·20
90	1·450	55·03		1·8390	99·70
93	1·465	56·43		1·8384	100·00
96	1·480	57·83			

The acid is not a single chemical individual, but consists of a solution of sulphur trioxide and disulphuric acid, $H_2S_2O_7$, in varying proportions in sulphuric acid. When the strong fuming acid is cooled, *disulphuric acid* or *pyrosulphuric acid*, $H_2S_2O_7$ or $O(SO_2.OH)_2$, separates out in white crystals, melting at 35°, which fume strongly in the air and readily decompose into sulphuric acid and the trioxide on warming. This acid may also be prepared by mixing the ordinary acid and trioxide in the necessary proportions. Disulphuric acid forms a stable series of salts, sodium disulphate being formed when sodium hydrogen sulphate is heated so long as water is evolved:—

$$2HO.SO_2.ONa = O(SO_2.ONa)_2 + H_2O.$$

When still more strongly heated it decomposes into sulphur trioxide and normal sodium sulphate.

The strength of fuming sulphuric acid is usually expressed by stating the percentage of "free" SO_3, that is to say, SO_3 which is not in combination with water forming sulphuric acid. The following table gives the specific gravity of varying strengths of the fuming acid.[1]

Total SO_3 per cent.	Free SO_3 per cent.	Sp. gr. at 15°	Sp. gr. at 45°
81·63	0·0	1·850	1·822
83·46	10·0	1·888	1·858
85·30	20·0	1·920	1·887
87·14	30·0	1·957	1·920
88·97	40·0	1·979	1·945
90·81	50·0	2·009	1·964
92·65	60·0	2·020	1·959
94·48	70·0	2·018	1·942
96·32	80·0	2·008	1·890
98·16	90·0	1·990	1·864
100·00	100·0	1·984	1·814

The boiling point decreases with increasing percentage of SO_3, acid containing 3·64 per cent. of free SO_3 boiling at 212° under 759 mm. pressure, whilst acid containing 63·2 per cent. boils at 60°. Samples containing less than 30 per cent., or between 60 and 70 per cent. of free SO_3, are liquid at the ordinary temperature, the remainder being solid, but becoming liquid at temperatures not exceeding 36°.

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[1] Knietsch, *Ber.* 1901, , 4101.

Fuming sulphuric acid is employed in very large quantities in the Coal Tar Colour Industry.

Sulphur trioxide and sulphuric acid also unite together to form *tetra-sulphuric acid*, $3SO_3 + H_2SO_4 = H_2S_4O_{13}$, an oily liquid, and another compound, having the composition $SO_3 + 3H_2SO_4$, a transparent crystalline mass melting at 26°.

HALOGEN DERIVATIVES OF SULPHURIC ACID.

246 *Fluosulphonic acid*, $F.SO_2.OH$, is obtained by the action of an excess of hydrogen fluoride on sulphur trioxide contained in a platinum vessel cooled by ice and calcium chloride, the excess of hydrogen fluoride being removed by a current of carbon dioxide at 25–35°. It forms a colourless mobile liquid, which boils with slight decomposition at 162·6°, has a slight pungent smell, and is greasy to the touch. It has but little action on dry skin, but slowly attacks glass, especially in presence of moist air. It is decomposed almost explosively by water, forming sulphuric and hydrofluoric acids.[1]

Sulphuryl fluoride, SO_2F_2, is obtained by passing fluorine into dry sulphur dioxide, the former gas passing over an electrically heated platinum wire just before the point of issue, and is also formed as one of the products of the action of fluorine on moist sulphuretted hydrogen. The gas obtained in the first-named manner is washed with water and copper sulphate solution, dried over anhydrous potassium fluoride, and purified by liquefaction and fractionation. It is thus obtained as a colourless inodorous gas, which on compression yields a liquid boiling at −52° and solidifying at −120°. Like sulphur hexafluoride, it is an extremely stable substance, and is not decomposed below a red heat. It dissolves in 10 parts of water at 9°, and is slowly absorbed by aqueous alkalis, rapidly by the alcoholic solutions. With ammonia at the ordinary temperature it yields the white solid compound $SO_2F_2.5NH_3$, which is soluble in water.[2]

Chlorosulphonic acid, $Cl.SO_2.OH$, was first obtained by Williamson[3] by the direct union of sulphur trioxide and hydrochloric acid gas, and now that sulphur trioxide is so cheaply

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[1] Thorpe and Kirman, *Journ. Chem. Soc.* 1892, 921.

[2] Moissan and Lebeau, *Compt. Rend.* 1901, **132**, 374.

[3] *Proc. Roy. Soc.* 1856, **7**, 11.

manufactured, is best prepared in this way. It may also be prepared by the distillation of a mixture of concentrated sulphuric acid and phosphorus pentachloride or oxychloride :—

$$2H_2SO_4 + POCl_3 = 2Cl.SO_2.OH + HPO_3 + HCl.$$

It is a colourless liquid, which fumes strongly in the air, has a specific gravity of 1·766 at 18°, and boils at 152–153°. When heated under pressure at 170–190° it undergoes partial decomposition into sulphuric acid and sulphuryl chloride, and at higher temperatures sulphur dioxide, chlorine and water vapour are formed.[1] In presence of many metallic salts, especially those of mercury, the first-named decomposition takes place much more readily.

Chlorosulphonic acid decomposes water with explosive violence, yielding sulphuric and hydrochloric acids.

Sulphuryl Chloride, SO_2Cl_2.—This substance was first obtained by Regnault in 1838, mixed with ethylene chloride, by the action of chlorine on a mixture of ethylene and sulphur dioxide,[2] and is also formed when a solution of the two gases in acetic acid is allowed to stand. It is, however, most easily prepared from chlorosulphonic acid, which, as mentioned in the previous paragraph, decomposes on heating, especially in presence of catalytic agents, into sulphuryl chloride and sulphuric acid :—

$$2Cl.SO_2.OH = SO_2Cl_2 + SO_2(OH)_2.$$

To prepare it chlorosulphonic acid, mixed with 1 per cent. of mercuric sulphate, is boiled, and the vapours evolved passed first through a reflux condenser kept at about 70°, the sulphuryl chloride vapour passing through this without liquefying, and being condensed by means of a second condenser.[3]

Sulphuryl chloride is a colourless, strongly pungent smelling liquid, which boils at 69·1—69·2°, and has a specific gravity of 1·66738 at 20°/4°.[4] It has a normal vapour density at 130°, but dissociation of the vapour commences below 160°, and is considerable at 240–250°.

Sulphuryl chloride combines with ice-cold water to form a hydrate, probably having the formula $SO_2Cl_2,15H_2O$; this

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[1] Ruff, *Ber.* 1901, **34**, 3509.

[2] *Ann. Chim. Phys.* 1838, (2), **69**, 170.

[3] Ruff, *Ber.* 1901, **34**, 3511; Wohl and Ruff, *Journ. Chem. Soc.* 1902, ii. 604.

[4] Pawlewski, *Ber.* 1897, **30**, 765.

resembles camphor in appearance, it is sparingly soluble in water at 0°, and in small quantity is unaltered on remaining in water at 0° for hours; it is also stable in presence of sodium hydrogen carbonate.[1] At somewhat higher temperatures it is converted by a small quantity of water into chlorosulphonic acid and hydrochloric acid, and with a larger quantity into sulphuric and hydrochloric acids.

The chlorine in sulphuryl chloride is somewhat feebly combined, and it is therefore sometimes employed in organic chemistry as a chlorinating agent.

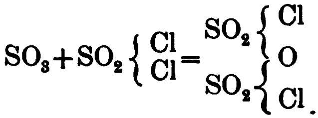
Disulphuryl Chloride, $S_2O_5Cl_2$.—The chloride of disulphuric acid was first prepared by Rose[2] by the action of chloride of sulphur on sulphur trioxide, thus:—

$$S_2Cl_2 + 5SO_3 = S_2O_5Cl_2 + 5SO_2.$$

The same compound has also been obtained by Michaelis[3] by heating sulphur trioxide with phosphorus oxychloride; thus:—

$$6SO_3 + 2POCl_3 = 3S_2O_5Cl_2 + P_2O_5.$$

It is likewise formed when common salt is heated with sulphur trioxide, and when this latter substance is brought in contact with sulphuryl chloride; thus:—



$$SO_3 + SO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. = \begin{matrix}SO_2\\ \\SO_2\end{matrix}\left\{\begin{matrix}Cl\\O\\Cl\end{matrix}\right..$$

It is a colourless fuming liquid, boiling at 142° under 765 mm., and at 53° under 15 mm. pressure; it has a specific gravity at 18° of 1·819, and solidifies at a low temperature to a crystalline solid, melting at −39°. Water decomposes it into sulphuric acid and hydrochloric acid.

Sulphur Oxytetrachloride, $S_2O_3Cl_4$.—Millon first obtained this substance by the action of moist chlorine upon sulphur or chloride of sulphur. It is best prepared by cooling down a mixture of chloride of sulphur and chlorosulphonic acid to −15°, and then saturating the liquid with chlorine, when the following reaction takes place:—

$$SO_3HCl + SCl_4 = S_2O_3Cl_4 + HCl.$$

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[1] Baeyer and Villiger, *Ber.* 1901, **34**, 736.

[2] *Pogg. Ann.* 1838, **44**, 291.

[3] *Zeitsch. Chem.* 1871, **7**, 149.

Sulphur oxytetrachloride forms a white crystalline mass, which has a very pungent smell and attacks the mucous membrane violently. It dissolves in water with a hissing noise, forming hydrochloric, sulphuric, and sulphurous acids. Exposed to moist air, it deliquesces with evolution of chlorine, hydrochloric acid, and sulphur dioxide, leaving a residue of thionyl chloride and disulphuryl chloride. When the compound is heated it partially sublimes in fine white needles, whilst another portion decomposes into sulphur dioxide, chlorine, thionyl chloride, and disulphuryl chloride. When kept in closed tubes this body liquefies with the formation of thionyl and sulphuryl chlorides; thus:—

$$S_2O_3Cl_4 = SOCl_2 + SO_2Cl_2.$$

No bromine or iodine derivatives of sulphuric acid are yet definitely known. A white solid substance was stated by Odling and Abel[1] to be formed by the union of sulphur dioxide and bromine, but later observers[2] have not confirmed this.

SULPHUR SESQUIOXIDE. S_2O_3.

247 So long ago as the year 1804 Buchholz found that when sulphur is heated with fuming sulphuric acid an intensely blue-coloured solution is formed, and in the year 1812 F. C. Vogel showed that this blue body is also produced by the action of sulphur on sulphur trioxide. In later years this subject frequently attracted the attention of chemists, but the nature of the blue substance remained unexplained until R. Weber[3] showed that it consists of a new oxide of sulphur.

In order to prepare this substance, carefully dried flowers of sulphur are added, in small quantities, to recently prepared and liquid sulphur trioxide, a fresh quantity of sulphur only being added when that already present has entered into combination. In order to moderate the reaction, the test-tube in which the solution is made must be placed in water at a temperature of from 12° to 15°. The sulphur on falling into the trioxide dissolves in the form of blue drops which sink down to the bottom of the test-tube and then solidify. As soon as a sufficient quantity of this substance has been formed, the supernatant

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[1] Odling, *Journ. Chem. Soc.* 1855, 2.

[2] Michaelis, *Lehrbuch*, i. 733 (5th Edition).

[3] *Pogg. Ann.* 1875, **156**, 531.

sulphur trioxide is poured off and the residue removed from the test-tube by very gently warming it.

Sulphur sesquioxide forms bluish-green crystalline crusts, in colour closely resembling malachite. At the ordinary temperature it slowly decomposes into sulphur dioxide and free sulphur, and this decomposition takes place more readily when the substance is warmed; thus :—

$$2S_2O_3 = 3SO_2 + S.$$

This compound dissolves in fuming sulphuric acid, giving rise to a blue solution which on the addition of common sulphuric acid gradually assumes a brown colour. Water decomposes the sesquioxide with the separation of sulphur and the formation of sulphuric acid, sulphurous acid, and thiosulphuric acid.

Sulphur sesquioxide from its composition would appear to be the anhydride of hyposulphurous acid, but neither of these substances has yet been converted into the other.

HYPOSULPHUROUS ACID. HSO_2 or $H_2S_2O_4$.

248 Berthollet in 1789 showed that iron dissolves in aqueous sulphurous acid without evolution of gas, and Fourcroy and Vauquelin in 1798 found that zinc and tin act in a similar manner. Schönbein[1] in 1852 recognised the existence of a lower sulphur acid in the solution, and observed its reducing power on indigo, but his results were forgotten, and the acid and salts rediscovered by Schützenberger[2] in 1869. As neither acid nor salts were obtained even approximately pure, much uncertainty prevailed as to their exact composition. Schützenberger termed the acid *hydrosulphurous acid* and assigned to it the formula H_2SO_2, the sodium salt being regarded as $NaHSO_2$, whilst Bernthsen[3] showed that the formula was probably HSO_2 or the double formula $H_2S_2O_4$, that of the sodium salt being $NaSO_2$ or $Na_2S_2O_4$. This view has been confirmed by the isolation of the sodium and zinc salts in a state of purity, the composition of which agrees with the above formula. No determination of the molecular weight of the salts has yet been made, but from analogy with thiosulphuric acid, the doubled formula is usually employed, although the fact that no acid

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[1] *Verh. Basler. Nat. Forsch. Ges.*, 17 Nov. and 19 Dec. 1852.

[2] *Compt. Rend.* 1869, **69**, 169.

[3] *Annalen*, 1881, **208**, 142; 1882, **211**, 285.

salts have been prepared is more in favour of the simple formula.

When zinc is allowed to act on a solution of hydrogen sodium sulphite in closed vessels, no hydrogen is evolved, but a mixture of sulphites and hyposulphites of sodium and zinc is obtained, from which the latter cannot be isolated in a state of purity. If, however, the sodium hydrogen sulphite be previously mixed with half its equivalent of sulphurous acid, a reaction takes place which may be expressed as follows:

$$Zn + 2NaHSO_3 + H_2SO_3 = Na_2S_2O_4 + ZnSO_3 + 2H_2O.$$

When treated with the requisite quantity of milk of lime in absence of air, the whole of the zinc, sulphurous acid, and calcium is precipitated, and the filtrate consists of a solution of sodium hyposulphite. On adding sodium chloride to the warm fairly concentrated solution and cooling, pure sodium hyposulphite crystallises out in thin vitreous prisms, having the composition $Na_2S_2O_4,2H_2O$. These are freed from mother-liquor by washing, first with aqueous, and finally with anhydrous acetone, and dried over sulphuric acid.[1] The salt thus obtained is fairly stable in dry air, but rapidly oxidises in moist air, with formation of sodium metabisulphite:

$$2Na_2S_2O_4 + O_2 = 2Na_2S_2O_5,$$

whilst the aqueous solution even in absence of air undergoes decomposition, sodium thiosulphate being one of the products.

Zinc hyposulphite is formed by the action of zinc on a solution of sulphur dioxide:

$$Zn + 2SO_2 = ZnS_2O_4.$$

To obtain the pure salt, dry sulphur dioxide is passed into a flask which contains zinc and absolute alcohol, and from which the air has been removed; a white precipitate gradually forms and is removed after 24 hours and more sulphur dioxide is then passed in, the process being repeated until a sufficient quantity has been prepared.[2] After drying over sulphuric acid to remove alcohol of crystallisation, the white salt has the composition ZnS_2O_4.

Sodium hyposulphite is also formed by the electrolysis of a solution of sodium hydrogen sulphite.

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[1] Bernthsen and Basler, *Ber.* 1900, **33**, 126.

[2] Nabl, *Monatsh.* 1899, **20**, 679.

An aqueous solution of hyposulphurous acid is formed by adding dilute oxalic acid solution to one of sodium hyposulphite; the yellow liquid thus obtained rapidly changes, thiosulphuric acid being first formed, which then quickly decomposes, forming sulphurous acid and sulphur.

On account of its very great affinity for oxygen, sodium hyposulphite is employed as a reducing agent, being especially used by the calico-printer and dyer for the reduction of indigo, and it is also employed for the estimation of dissolved oxygen in water, (p. 316).

SULPHUR HEPTOXIDE, S_2O_7, AND THE PERSULPHURIC ACIDS.

249 When a mixture of dry oxygen and sulphur dioxide is subjected to the action of the silent electrical discharge, combination takes place and sulphur heptoxide is produced.[1] The anhydrous substance is a viscid liquid which solidifies at 0°, forming granules, needles, or scales. It is readily volatile, and gradually decomposes on keeping, and rapidly on heating, into sulphur trioxide and oxygen. When brought into water it combines with it violently with a hissing noise and evolution of so much heat, that a considerable proportion of the acid produced is decomposed into oxygen and sulphuric acid.

Faraday in 1832 observed that in the electrolysis of strong solutions of sulphuric acid, the oxygen evolved is considerably less than one-half of the hydrogen simultaneously produced, but the absorption of oxygen was not accounted for until the publication of the above work by Berthelot, who showed that in the electrolysis a persulphuric acid is produced which is similar to that obtained by acting on the heptoxide with water, and may also be prepared by treating hydrogen dioxide with strong solutions of sulphuric acid. He was unable to isolate the acid, but recognised that the solution contained more than one substance possessing oxidising properties. In 1891 Marshall succeeded in isolating the persulphates, $M_2S_2O_8$, corresponding to sulphur heptoxide, these being obtained as well defined crystalline salts by the electrolysis of the acid sulphates of the metals,[2] and it was then generally supposed that the acid solutions prepared by Berthelot consisted of the corresponding persulphuric acid, $H_2S_2O_8$.

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[1] Berthelot, *Ann. Chim. Phys.* 1878, [5], **14**, 345, 363.

[2] *Journ. Chem. Soc.* 1891, 771.

In 1898, however, Caro[1] observed that the solution obtained by acting on a persulphate with concentrated sulphuric acid differs totally in its oxidising action on aniline from that obtained when dilute acid is used, so that the solution obtained in the former manner must contain an oxidising agent differing from persulphuric acid. This solution was largely employed as an oxidising agent for organic substances, and as its constitution was unknown it was termed *Caro's acid.*

Since then the subject has been studied by many investigators, and much light has been thrown on the matter, although, as none of the acids present, and, with the exception of Marshall's persulphates, none of the corresponding salts have been isolated in a pure state, conclusive results have not yet been obtained.

The primary product of the action of sulphuric acid on a persulphate, or on hydrogen dioxide, or of the electrolysis of strong solutions of sulphuric acid, appears to be persulphuric acid, $H_2S_2O_8$, but this acid in presence of sulphuric acid containing only small quantities of water, rapidly undergoes partial hydrolysis, yielding Caro's acid and sulphuric acid. Baeyer and Villiger[2] have devised a method by which the amount of each of these acids and of hydrogen dioxide, if present, can be estimated with fair accuracy, depending on the facts that the last of these is the only one which reduces potassium permanganate immediately, and that the two former differ in their action on potassium iodide, Caro's acid liberating iodine from it immediately, whilst persulphuric acid only does so slowly, twenty-four hours being required for the completion of the reaction.

By this method they found that the ratio of "peroxide" oxygen to SO_3 in Caro's acid is such that for each atom of this "peroxide" oxygen one molecule of SO_3 is present, whence they concluded that the acid has the formula H_2SO_5, and that it is *permonosulphuric acid*, $HO.SO_2.O.OH$. A neutralised solution of such an acid should on losing its additional atom of oxygen yield a neutral sulphate solution, whereas Armstrong and Lowry[3] have shown that under these circumstances the solution, in addition to the neutral sulphate, contains one molecule of free sulphuric acid for each atom of "peroxide" oxygen lost, and they suggest that Caro's acid is an "anhydro" derivative $H_2S_2O_9$, standing in the same

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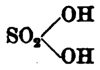
[1] *Zeit. angew. Chem.* 1898, 845.

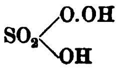
[2] *Ber.*, 1901, **34**, 853.

[3] *Proc. Roy. Soc.* 1902, **70**, 94.

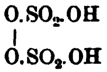
relation to an acid of the constitution assumed by Baeyer and Villiger as sulphuric to disulphuric acid.



Sulphuric Acid.

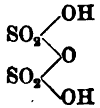


Permonosulphuric Acid.

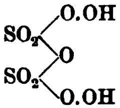


$$\begin{array}{c} O.SO_2.OH \\ | \\ O.SO_2.OH \end{array}$$

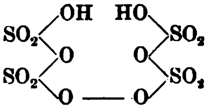
Persulphuric Acid.



Disulphuric Acid.



Anhydropermono-sulphuric Acid.



Pertetrasulphuric Acid.

The formula $H_2S_2O_9$ has been further confirmed by the investigations of Price[1] and Mugdan.[2]

It is found that the stronger the sulphuric acid, the greater is the proportion of Caro's acid produced. Lowry and West[3] have further proved that the ratio of total "peroxide" oxygen to SO_3 in any solution, whether obtained by the action of sulphuric acid on hydrogen dioxide or by electrolysis, depends entirely on the ratio of water to sulphuric acid.

When the proportion of water to sulphuric acid in the solutions prepared in any of the ways mentioned is small it seems probable that these in addition to Caro's acid and persulphuric acid, contain *pertetrasulphuric acid,* $H_2S_4O_{14}$, which stands in the same relation to disulphuric acid as persulphuric to sulphuric acid[4] (see constitutional formulæ above).

Caro's acid, or *Anhydropermonosulphuric acid,* $O(SO_2.O.OH)_2$, is only known in solution and has not been obtained free from sulphuric and persulphuric acid. A solution containing 16 parts of persulphuric acid for every 84 parts of Caro's acid is obtained by triturating 10 grams of potassium persulphate with 20 grams of concentrated sulphuric acid, allowing to stand for an hour, pouring on to ice, and removing free sulphuric acid by treatment with barium phosphate. The solution containing phosphoric acid is fairly stable, as is also a solution containing 8 per cent. of sulphuric acid and only very slowly undergoes hydrolysis into sulphuric acid and hydrogen dioxide. (Baeyer and Villiger.)

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[1] *Journ. Chem. Soc.* 1903, 543.

[2] *Zeit. Electrochem.* 1903, 7, 719.

[3] *Journ. Chem. Soc.* 1900, 950.

[4] Armstrong and Lowry, *loc. cit.*

Persulphuric acid, $(O.SO_2OH)_2$, is obtained in solution by decomposing barium persulphate with exactly the necessary quantity of dilute sulphuric acid. It slowly changes, even when pure, forming Caro's acid and sulphuric acid, and in presence of strong acid the change is, as already stated, very rapid.

The *potassium* salt, $K_2S_2O_8$, is obtained by passing a current of 3 to 3½ amperes through a saturated solution of potassium hydrogen sulphate, contained in a platinum basin and cooled externally by water; the dish is connected with the positive pole, the negative pole consisting of a platinum wire placed in a porous cell which is filled with dilute sulphuric acid and suspended in the solution of potassium hydrogen sulphate. The salt separates out in the course of 24–48 hours as a mass of white crystals, which on recrystallising form large tabular, apparently triclinic crystals. It is very sparingly soluble in water, 100 parts of the latter at 0° dissolving 1·77 parts of the salt, yielding a neutral solution. From the conductivity of the solution the molecular formula appears to be $K_2S_2O_8$ and not KSO_4. The solution slowly decomposes with evolution of oxygen on preservation, the action being greatly accelerated by heat, whilst the dry salt on heating loses oxygen and sulphur trioxide leaving a residue of potassium sulphate.

The *ammonium* salt, $(NH_4)_2S_2O_8$, is prepared in a similar manner to the potassium salt, and forms lozenge shaped, apparently monoclinic tablets, and differs from the latter in being very soluble in water, 100 parts of water at 0° dissolving 58·2 parts of the salt. The *barium* salt, $BaS_2O_8,4H_2O$, is also very soluble in water, whilst the *lead* salt, PbS_2O_8, is deliquescent.

All the persulphates hitherto prepared are soluble in water, the potassium salt being the least soluble. The solutions have strong oxidising properties, rapidly oxidising ferrous to ferric salts, and yielding precipitates of the higher oxides of the metals when warmed with solutions of silver, copper, manganese, cobalt and nickel salts, but they only liberate iodine slowly from potassium iodide (p. 443). When warmed with hydrochloric acid, chlorine is evolved.

Ammonium persulphate is now manufactured on the large scale for use as an oxidising agent, especially in technical organic chemistry.

THIOSULPHURIC ACID. $H_2S_2O_3$.

250 This compound is sometimes known under its old name of "hyposulphurous acid," with which name, however, we now designate the body obtained by the reduction of sulphurous acid. Thiosulphuric acid has not been isolated in the free state, but it forms a series of stable salts which are known as the thiosulphates (hyposulphites). When a dilute acid is added to a solution of a thiosulphate, the solution remains, to begin with, perfectly clear; but sulphur soon begins to separate out as a white, very finely divided powder, and the solution is found to contain sulphurous acid, sulphur dioxide being also evolved; the thiosulphuric acid undergoes on liberation the following decomposition:—

$$H_2S_2O_3 = H_2O + SO_2 + S.$$

This decomposition is quantitative when the sulphur dioxide is removed from the solution, but when it is retained, a limit short of complete decomposition is attained, and other products, probably tri- and tetra-thionic acids, are formed.[1]

The delay in the appearance of the precipitate of sulphur is due to the time required for the sulphur to form visible aggregates, the decomposition of the acid commencing immediately upon its liberation.[2]

The rate of decomposition of the acid varies with the concentration of the hydrogen ions present in the solution.[3]

Thiosulphuric acid is formed in small amount by the action of sulphurous acid upon flowers of sulphur at the ordinary temperature, more rapidly at 80—90°.[4]

The thiosulphates are formed in various ways: thus, for instance, sodium thiosulphate (formerly called hyposulphite of soda), which was first prepared by Chaussier in 1799, but afterwards more carefully examined by Vauquelin, is formed when sulphur dioxide is passed into a solution of sodium sulphide; thus:—

$$(a)\ SO_2 + H_2O + Na_2S = Na_2SO_3 + SH_2.$$
$$(b)\ SO_2 + 2SH_2 = 2H_2O + 3S.$$
$$(c)\ Na_2SO_3 + S = Na_2S_2O_3.$$

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[1] Colefax, *Journ. Chem. Soc.* 1892, 176.

[2] Holleman, *Rec. Trav. Chim.* 1895, **14**, 71; *Zeit. physikal. Chem.* 1900, **33**, 500.

[3] v. Oettingen, *Zeit. physikal. Chem.* 1900, **33**, 1.

[4] *Journ. Chem. Soc.* 1892, 199; Aloy, *Compt. Rend.* 1903, **137**, 51.

The same salt is also formed according to equation (*c*) when a solution of sodium sulphite is boiled with flowers of sulphur and this is the method by which the salt is usually prepared (Vauquelin). Sodium thiosulphate is also formed when the requisite amount of iodine is added to a solution of sodium sulphite and sodium sulphide; thus:[1]—

$$Na_2SO_3 + Na_2S + I_2 = Na_2S_2O_3 + 2NaI.$$

Thiosulphates are also produced by the oxidation of sulphides, either by the oxygen of the air or by means of suitable oxidising agents.

These various methods of preparation point out that thiosulphuric acid is formed by the addition of sulphur to sulphurous acid, just as sulphuric acid is formed by the addition of oxygen to the same substance. Thiosulphuric acid may, therefore, be regarded as sulphuric acid in which one atom of oxygen is replaced by sulphur, and its formula is accordingly $SO_2\left\{\begin{matrix}OH.\\SH.\end{matrix}\right.$ The decompositions which its salts undergo bear out this interpretation of its constitution.[2] Thus the decomposition of the free acid into sulphur and sulphurous acid has already been mentioned; and when a solution of sodium thiosulphate is treated with sodium amalgam, sodium sulphite and sodium sulphide are formed (Spring); thus:—

$$Na_2S_2O_3 + 2Na = Na_2SO_3 + Na_2S.$$

Again, when silver thiosulphate is warmed with water, black sulphide of silver separates out, and the solution contains free sulphuric acid; thus:—

$$SO_2\left\{\begin{matrix}OAg\\SAg\end{matrix}\right. + H_2O = Ag_2S + SO_2\left\{\begin{matrix}OH.\\OH\end{matrix}\right.$$

And, moreover, when a solution of sodium thiosulphate is treated with cobalt chloride, black sulphide of cobalt is precipitated; thus:—

$$SO_2\left\{\begin{matrix}ONa\\SNa\end{matrix}\right. + CoCl_2 + H_2O = SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. + CoS + 2NaCl.$$

This formula is also borne out by the fact that the isomeric sodium potassium sulphites (p. 397) are converted by the action

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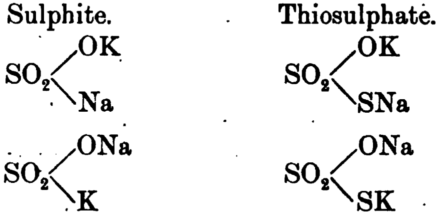
[1] Spring, *Ber.* 1874, 7, 1157.

[2] Schorlemmer, *Journ. Chem. Soc.* 1869, 256.

of ammonium polysulphides into isomeric thiosulphates, which differ in solubility and specific gravity, and yield different products when acted upon by ethyl iodide.[1]



The soluble thiosulphates generally crystallise well, and contain water of crystallisation, the last molecule of which is very difficult to remove by heat, being generally lost at such a high temperature that the decomposition of the salt has already commenced. Hence it was formerly supposed that the thiosulphates all contained hydrogen.

The thiosulphates exhibit a great tendency to form double salts; those thiosulphates which are insoluble in water are found to dissolve in an aqueous solution of sodium thiosulphate, which also has the power of dissolving other insoluble salts, such as silver chloride, silver bromide, silver iodide, lead iodide, lead sulphate, calcium sulphate, &c.; thus:—

$$\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\} S_2O_3 + AgCl = \left.\begin{matrix}\mathrm{Na}\\\mathrm{Ag}\end{matrix}\right\} S_2O_3 + NaCl.$$

Sodium silver thiosulphate forms distinct crystals, having the composition $AgNaS_2O_3 + H_2O$, and these are distinguished by possessing a sweet taste. The use of sodium thiosulphate for fixing prints in photography, first suggested by Sir John Herschel, probably depends on the formation of this salt. The silver chloride with which the photographic paper is impregnated when exposed to the light becomes blackened, the chloride undergoing a chemical change, after which it is insoluble in sodium thiosulphate. In order, therefore, to fix such a photographic print, it is only necessary, after exposure to light, to soak the paper in a bath of the thiosulphate; the unaltered chloride of silver dissolves, and the picture, on washing, is found to be permanent. The removal of the silver bromide which remains unaltered after the development of an exposed gelatino-bromide plate depends on a similar action.

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[1] Schwicker, *Ber.* 1889, **22**, 1733.

Several other complex thiosulphates of silver and sodium are also known.

The thiosulphates are distinguished from the sulphites, inasmuch as when dilute hydrochloric acid or sulphuric acid is added to their solution not only is sulphur dioxide given off as a gas, but free sulphur is deposited as a white powder. On adding a thiosulphate solution to a lead salt, a white precipitate soluble in excess of the thiosulphate solution is produced, whilst with a silver or mercuric salt, a white precipitate of the insoluble thiosulphate is first thrown down, but this quickly becomes dark, and finally black, from its decomposition into a metallic sulphide and sulphuric acid. Solutions of mercurous salts give, with the thiosulphates, dense black precipitates, and when a thiosulphate is boiled with an ammoniacal solution of a ruthenium salt, the solution becomes of such an intensely dark red colour that in the concentrated condition it appears almost black. Ferric chloride added to a solution of a thiosulphate gives a dark violet coloration, which soon disappears, sulphur being deposited.

Sodium thiosulphate is largely used in volumetric analysis for the estimation of free iodine.

DITHIONIC ACID. $H_2S_2O_6$.

251 This acid, formerly called hyposulphuric acid, was discovered by Welter and Gay-Lussac in 1819. The manganese salt of the acid is prepared by passing sulphur dioxide into water containing manganese dioxide in suspension. A mixture of manganese dithionate and sulphate is thus produced, the reaction being somewhat complicated, and manganic sulphite being probably formed as an intermediate product;

(1) $2MnO_2+3H_2SO_3=Mn_2(SO_3)_3+3H_2O+O$.
(2) $Mn_2(SO_3)_3=MnSO_3+MnS_2O_6$.
(3) $MnSO_3+O=MnSO_4$.

Some sulphate is also probably produced directly,

$$MnO_2+SO_2=MnSO_4.$$

Ferric hydroxide is reduced in a similar manner, but in this case no sulphate is produced;

$$2Fe(OH)_3+3SO_2=Fe_2(SO_3)_3+3H_2O=FeS_2O_6+FeSO_3+3H_2O$$

Manganic hydroxide, MnO(OH), and cobaltic hydroxide, $Co(OH)_3$, on the other hand, yield a considerable proportion of sulphate, whilst pure nickelic hydroxide yields a mixture of sulphite and sulphate, no dithionate being formed.[1]

In order to obtain the dithionate free from sulphate, advantage is taken of the solubility of barium dithionate in water; baryta water, $Ba(OH)_2$, is added until all the metal is precipitated as manganese hydroxide, $Mn(OH)_2$, and all the sulphuric and sulphurous acids are thrown down as insoluble barium salts; on evaporating and cooling, barium dithionate, $BaS_2O_6 + 2H_2O$, crystallises out, and when this is decomposed by the requisite quantity of dilute sulphuric acid, a solution of dithionic acid is obtained. This solution may be concentrated *in vacuo* over sulphuric acid until it has a specific gravity of 1·347, but on attempting to concentrate it further, the acid is resolved into sulphur dioxide and sulphuric acid; thus:—

$$H_2S_2O_6 = SO_2 + H_2SO_4.$$

Dithionic acid is also formed in small quantity by the oxidation of sulphurous acid by means of potassium permanganate.[2]

In order to obtain the salts of this acid we may add the corresponding base to the acid solution, or they may be obtained more simply by adding a soluble sulphate to barium dithionate. Dithionates are also produced by the electrolysis of a neutral or alkaline solution of a sulphite.[3] Only the normal salts are known, most of which crystallise well, and they contain, with the exception of the potassium salt, water of crystallisation. Their aqueous solutions are not oxidised in the cold either by atmospheric oxygen, by nitric acid, or by potassium permanganate; though when they are heated with these oxidising agents they are converted into the sulphates. On heating they decompose partially at 100°, and entirely at a higher temperature, into sulphur dioxide, and a sulphate which remains behind; when sodium amalgam is added to a solution

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[1] Meyer, *Ber.* 1901, **34**, 3606; 1902, **35**, 3429; Carpenter, *Journ. Chem. Soc.* 1902, 1.

[2] *Ann. Chim. Phys.* 1859 (3), **55**, 374. Dymond and Hughes, *Journ. Chem. Soc.* 1897, 314.

[3] Friessner, *Zeit. Elektrochem.* 1904, **10**, 265.

of sodium dithionate, two molecules of sodium sulphite are formed (R. Otto); thus:—

$$\begin{array}{l} SO_2.ONa \\ \vert \\ SO_2.ONa \end{array} + 2Na = \begin{array}{l} Na.SO_2.ONa. \\ \\ Na.SO_2.ONa. \end{array}$$

The dithionates are distinguished from the thiosulphates, inasmuch as they evolve sulphurous acid when heated with hydrochloric acid without separation of sulphur, whilst the solution afterwards contains a sulphate.

Trithionic Acid. $H_2S_3O_6$.

252 In 1842, Langlois obtained the potassium salt of this acid by gently heating a solution of acid potassium sulphite with sulphur; thus:—

$$S_2 + 6KHSO_3 = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

The same salt is also produced when a solution of potassium thiosulphate is saturated with sulphur dioxide; thus:—

$$3SO_2 + 2K_2S_2O_3 = 2K_2S_3O_6 + S.$$

It is best prepared by treating a saturated solution of potassium thiosulphate with gaseous sulphur dioxide until it is yellow, allowing to stand until the colour disappears and then again passing in sulphur dioxide. The potassium salt soon crystallises out and may be recrystallised from lukewarm water.

Further changes also occur, the trithionate combining with the sulphur which is liberated to form tetra- and penta-thionate of potassium (Debus). The potassium salt is, moreover, formed when potassium silver thiosulphate is heated with water; thus:—

$$2SO_2\left\{\begin{array}{l} OK \\ SAg \end{array}\right. = Ag_2S + K_2S_3O_6.$$

A solution of the trithionate treated with sodium amalgam or caustic potash, decomposes into sulphite and thiosulphate.

Sodium trithionate is not, however, formed as a primary product by the action of iodine on a mixture of these salts, as stated by Spring, a sulphate and a tetrathionate being produced.[1]

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[1] Colefax, *Journ. Chem. Soc.* 1892, 1083.

In order to prepare free trithionic acid, hydro-fluosilicic acid is added to a solution of the potassium salt, when the insoluble hydro-fluosilicate of potassium is precipitated. The aqueous acid thus obtained has no smell, but has a strong acid and bitter taste; it may be concentrated in a vacuum up to a certain point, but it is an unstable compound, and at the ordinary temperature easily decomposes even in dilute solution into sulphur, sulphur dioxide, and sulphuric acid. The only one of the trithionates which is well known is the potassium salt. This on heating decomposes into sulphur, sulphur dioxide and potassium sulphate and its solution undergoes the same decomposition on standing:—

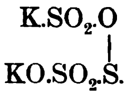
$$K_2S_3O_6 = K_2SO_4 + SO_2 + S.$$

In this case again secondary reactions occur, tetra- and pentathionates being formed by the combination of the trithionate with the sulphur. Its solution is not precipitated by barium chloride in the cold, though on heating barium sulphate separates out and sulphur dioxide is evolved, whilst silver nitrate gives a yellow precipitate which very quickly becomes black on standing.

Sulphuretted hydrogen has no action upon solutions of the free acid, but decomposes the potassium salt with formation of sulphate and thiosulphate of potassium and deposition of sulphur (Debus):

$$2K_2S_3O_6 + 5H_2S = K_2SO_4 + K_2S_2O_3 + 5H_2O + 8S.$$

The constitutional formula of potassium trithionate is probably the following (Debus):



$$\begin{array}{r}K.SO_2.O\\ |\\ KO.SO_2.S.\end{array}$$

TETRATHIONIC ACID. $H_2S_4O_6$.

253 Fordos and Gélis in 1843 first prepared this acid and its salts. They obtained the sodium salt by adding iodine to an aqueous solution of sodium thiosulphate; thus:—

$$\begin{array}{l}SO_2\left\{\begin{array}{l}ONa\\ SNa\end{array}\right.\\ SO_2\left\{\begin{array}{l}ONa\\ SNa\end{array}\right.\end{array} + I_2 = \begin{array}{l}SO_2\left\{\begin{array}{l}ONa\\ S\\ O\\ SNa\end{array}\right. \\ SO_2 \end{array}\!\!\left.\begin{array}{l}\\ \\ \end{array}\right\} + 2NaI.$$

Salts of this acid are also formed by the action of copper sulphate upon barium thiosulphate, by the action of sulphuric acid upon a mixture of lead thiosulphate, and peroxide, and by the electrolytic oxidation of thiosulphates.[1] In order to prepare the free acid, iodine in excess is added very gradually to thiosulphate of barium suspended in a very small quantity of water, the iodide of barium and excess of iodine being removed by shaking up the semi-solid mass with strong alcohol, leaving a white crystalline mass of barium tetrathionate, BaS_4O_6. This may then be dissolved in a small quantity of water and recrystallised, whilst from this pure salt the acid may be prepared by adding exactly sufficient sulphuric acid to decompose it completely.

Tetrathionic acid is a colourless, inodorous, very acid liquid, which, when dilute, may be boiled without undergoing decomposition, but in the concentrated state is easily decomposed into sulphurous and sulphuric acids and sulphur. The tetrathionates are all soluble in water, but their solutions cannot, as a rule, be evaporated without decomposition into sulphur and a trithionate. A solution of the potassium salt decomposes gradually on preservation, sulphur dioxide being evolved but no sulphur deposited. The decomposition proceeds in two stages, tri- and penta-thionate of potassium being first formed, and the trithionate then decomposing in the usual way into potassium sulphate, sulphur dioxide and sulphur, which converts a portion of the trithionate into pentathionate. (Debus.)

$$(1)\ 2K_2S_4O_6 = K_2S_3O_6 + K_2S_5O_6.$$
$$(2)\ 3K_2S_3O_6 = 2K_2SO_4 + 2SO_2 + K_2S_5O_6.$$

Dry potassium tetrathionate undergoes no alteration on preservation. Sodium amalgam decomposes the compound into two molecules of thiosulphate, and the same decomposition occurs on the addition of potassium sulphide; thus:—

$$K_2S_4O_6 + K_2S = 2K_2S_2O_3 + S.$$

Potassium tetrathionate does not combine with ordinary sulphur, but combines with nascent sulphur to form a pentathionate. Thus the free acid is decomposed by an excess of sulphuretted hydrogen into water and sulphur:—

$$H_2S_4O_6 + 5H_2S = 6H_2O + 9S.$$

[1] Thatcher, *Zeit. physikal. Chem.* 1904, **47**, 691.

When, however, a slow current of sulphuretted hydrogen is passed into a solution of the potassium salt, the sulphur combines with a portion of the salt and forms potassium pentathionate. Sulphur dioxide reacts with potassium tetrathionate to form a trithionate and a pentathionate, the latter being probably produced by a secondary reaction from thiosulphuric acid, or its anhydride, S_2O_2, which, however, is unknown in the free state:—

$$K_2S_4O_6 + SO_2 = K_2S_3O_6 + S_2O_2.$$

PENTATHIONIC ACID. $H_2S_5O_6$.

254 Wackenroder, in 1845, was the first to draw attention to the existence of this acid in the liquid obtained by passing sulphuretted hydrogen into a solution of sulphur dioxide; the clear liquid obtained after the removal of the precipitated sulphur was looked upon by him and his successors as a solution of the acid in water. The reaction was represented by the equation:—

$$5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O.$$

Later observers succeeded in preparing crystalline pentathionates from this liquid and thus placed the existence of the acid beyond doubt. The investigations of Debus[1] have shown that the liquid in question, known as Wackenroder's solution, has a very complex composition, which varies according to the method of preparation. The liquid is best prepared by passing sulphuretted hydrogen slowly for two hours into 480 c.c. of a saturated solution of sulphurous acid at a temperature near 0°, allowing the whole to stand for two days in a closed bottle and repeating the operation until all the sulphurous acid has disappeared. The liquid is then filtered from the sulphur which has separated out, and is thus obtained as a semi-transparent milky fluid. The solution contains oily drops of sulphur in suspension and a considerable amount of sulphur in a soluble form (p. 376), which can be precipitated by the addition of potassium nitrate or by concentrating the fluid on the water-bath. The concentration of the clear liquid cannot be carried further than a sp. gr. of 1·32 in this way without evolution of

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[1] *Journ. Chem. Soc.* 1888, 278—357 (where references to the literature of the subject will be found).

sulphur dioxide and deposition of sulphur, but may be continued over sulphuric acid *in vacuo* beyond this point.

An analysis of the solution thus obtained (sp. gr. 1·32) shows that its composition is approximately that of pentathionic acid, $H_2S_5O_6$. When, however, the liquid is carefully treated with about one-half of an equivalent of caustic potash and then allowed to evaporate spontaneously, a mixture of potassium tetra- and penta-thionates is obtained. The mother liquor on evaporation yields a salt which contains more sulphur than a pentathionate, and is probably potassium hexathionate (p. 456). In addition to these substances, Wackenroder's solution, prepared in the manner described, contains sulphuric acid and traces of trithionic acid, the amount of which becomes much greater when an insufficient quantity of sulphuretted hydrogen is used.

The pentathionates are decomposed by caustic alkalis, sulphur being deposited and a tetrathionate formed, and they are therefore best prepared from Wackenroder's solution by treating it with the acetate of the metal and allowing the solution to evaporate spontaneously. In the case of the potassium salt the resulting mixture of tetrathionate and pentathionate can be separated by picking out the crystals of the two salts, which differ in form (Debus), or by bringing them into a mixture of xylene and bromoform of sp. gr. 2·2, in which the tetrathionate sinks and the pentathionate floats.[1] The *potassium salt*, $2K_2S_5O_6 + 3H_2O$, crystallises in short rhombic prisms or six-sided plates. It forms a clear, neutral solution in two parts of water and can be recrystallised from water at 50° made acid with a little sulphuric acid. The solution decomposes on standing, more rapidly on heating, sulphur being deposited and a tetrathionate formed, but is more stable in the presence of a little sulphuric acid;

$$H_2S_5O_6 = H_2S_4O_6 + S.$$

The salt itself decomposes on keeping if any moisture be present, but if dried by washing the fine powder with dilute alcohol, and then preserved over sulphuric acid, it remains unaltered for years. On ignition it is converted into potassium sulphate, sulphur dioxide, and sulphur:—

$$K_2S_5O_6 = K_2SO_4 + SO_2 + 3S.$$

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[1] Hertlein, *Zeit. physikal. Chem.* 1896, **19**, 287.

Potassium pentathionate is also formed when a slow current of sulphuretted hydrogen is passed into a solution of the tetrathionate (p. 454). The *barium salt*, $BaS_5O_6+3H_2O$, and the *copper salt*, $CuS_5O_6+4H_2O$, are also crystalline.

The pentathionates may be distinguished from the lower members of the series by the facts that ammoniacal silver nitrate solution produces a brown coloration which rapidly becomes darker, a black precipitate being finally formed, and that caustic potash produces an immediate precipitate of sulphur, tetrathionate being also formed, whilst ammonia only gives this reaction on standing. They are not affected by hydrochloric acid, ferric chloride or barium chloride.

A solution of pure pentathionic acid, prepared by the decomposition of the potassium salt, is converted by sulphuretted hydrogen into water and sulphur:—

$$H_2S_5O_6+5H_2S=6H_2O+10S,$$

whilst the potassium salt yields a thiosulphate and a trithionate:—

$$3K_2S_5O_6+3H_2S=K_2S_2O_3+2K_2S_3O_6+3H_2O+10S.$$

Sulphur dioxide reacts both with the acid and its salts to form trithionic acid and, probably, thiosulphuric anhydride (p. 454):—

$$H_2S_5O_6+2SO_2=H_2S_3O_6+2S_2O_2.$$

255 *Hexathionic acid*, $H_2S_6O_6$, is only known in the form of its potassium salt obtained from the mother liquors of potassium pentathionate. This salt, which has not been obtained in a perfectly pure state, forms a warty crust and yields an aqueous solution, which decomposes even in the presence of acid. It reacts with caustic potash and ammoniacal silver nitrate solution in the same way as the pentathionates, but gives an immediate precipitate of sulphur with ammonia.

FORMATION OF WACKENRODER'S SOLUTION.

256 It seems probable that in the preparation of Wackenroder's solution, the direct product is tetrathionic acid:

$$H_2S+3SO_2=H_2S_4O_6.$$

This substance is then acted upon by sulphurous acid with formation of trithionic acid and thiosulphuric anhydride, S_2O_2

(p. 454). Moreover, the tetrathionic acid is converted by the sulphuretted hydrogen into water and sulphur, and a number of secondary reactions then go on, by means of which the thiosulphuric anhydride gives up some of its sulphur to the tetrathionic acid, forming pentathionic acid, whilst the trithionic acid combines with nascent sulphur, forming tetra-, penta- and hexa-thionic acids.

When the action of the sulphuretted hydrogen is allowed to continue until all action is at an end, water and sulphur are found to be the final products:—

$$2H_2S + SO_2 = 2H_2O + 3S.$$

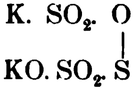
CONSTITUTION OF THE ACIDS OF WACKENRODER'S SOLUTION.

257 Potassium pentathionate is oxidised by bromine according to the following equation:—

$$K_2S_5O_6 + 4Br_2 + 6H_2O = 2KBr + 2S + 3H_2SO_4 + 6HBr.$$

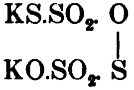
Hence two of the sulphur atoms are differently combined in the molecule from the other three; these two atoms are precipitated in the above reaction as free sulphur, whilst the other three are converted into sulphuric acid and are therefore probably already combined with oxygen in the molecule of pentathionic acid and in those of tetra- and tri-thionic acid, which stand in so close a relation to it. Trithionic acid moreover strongly resembles sulphurous acid in its power of combining with sulphur to form other acids and therefore probably contains the group $H.SO_2$, which is characteristic of sulphurous acid. The following formulæ exhibit all these relations and are also in accordance with the various decompositions of these substances;[1] they may therefore be assigned to the salts of these acids (Debus):—

Potassium Trithionate.



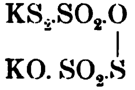
$$\begin{array}{l} K.\,SO_2.\,O \\ \qquad\quad\;\, | \\ KO.\,SO_2.\,S \end{array}$$

Potassium Tetrathionate.



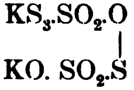
$$\begin{array}{l} KS.SO_2.\,O \\ \qquad\quad\;\, | \\ KO.SO_2.\,S \end{array}$$

Potassium Pentathionate.



$$\begin{array}{l} KS_2.SO_2.O \\ \qquad\quad\;\, | \\ KO.\,SO_2.S \end{array}$$

Potassium Hexathionate.



$$\begin{array}{l} KS_3.SO_2.O \\ \qquad\quad\;\, | \\ KO.\,SO_2.S \end{array}$$

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[1] Compare Hertlein, *Zeit. physikal. Chem.* 1896, **19**, 287.

SELENIUM. Se=78·6 (H=1); 79·2 (O=16).

258 We owe the discovery of this element to Berzelius.[1] He first found it in the deposit from the sulphuric acid chambers at Gripsholm in Sweden, in the year 1817, and it is to him that we are indebted for the knowledge of its most important compounds. The name selenium is derived from Σελήνη, the moon, on account of its analogy with the element tellurium (*tellus*, the earth), discovered shortly before.

Although selenium is somewhat widely distributed, it occurs only in small quantities. It is found together with sulphur in the islands of Volcano and Hawaii and in Japan, and occurs, chiefly combined with certain metals, at Clausthal and Zorge in the Harz, in La Plata, the Argentine and Mexico, as the mineral clausthalite, $PbSe$; a selenide of copper and lead, $PbSe + Cu_2Se$; lehrbachite, $PbSe + HgSe$; selenide of silver, Ag_2Se; selenide of copper, Cu_2Se. We also find it as onofrite, $HgSe + 4HgS$, in Mexico; whilst eucairite, $Cu_2Se + Ag_2Se$, and crookesite, $(CuTlAg)_2Se$, occur at Skrikerum in Sweden. Selenium is also found in very small quantity in meteoric iron, in some varieties of coal and in many other minerals, especially in certain iron-pyrites and copper-pyrites, and where these are used for the manufacture of sulphuric acid, a red deposit containing selenium is found in the flues and chambers.

Preparation.—In order to prepare selenium from this deposit, it is mixed with equal parts of sulphuric acid and water to a thin paste and then boiled, nitric acid or potassium chlorate being added until the red colour disappears. In this way a solution of selenic acid, H_2SeO_4, is obtained, which is diluted with water, filtered, and then heated with a quarter its volume of fuming hydrochloric acid until three-quarters of the liquid has evaporated. By this process chlorine is evolved and selenious acid, H_2SeO_3, formed. The cold solution is then poured off from the solid matter and saturated with sulphur dioxide, when selenium separates out as a red powder. The selenium thus obtained contains lead and other metals, from which it may be separated either by distillation or by being fused with a mixture of nitre and sodium carbonate, by which

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[1] *Schweigg Journ.* **23**, 309, 430; *Pogg. Ann.* 1826, **7**, 242; 1826, **8**, 423.

means sodium selenate is formed, and this is then again treated with hydrochloric acid and sulphur dioxide as above described (Wöhler).[1] Selenium may also be easily obtained from the chamber deposit by heating it on a water-bath with a concentrated solution of cyanide of potassium until it assumes a pure grey colour. On the addition of hydrochloric acid to the filtered solution selenium is deposited in cherry-red flakes. This deposit contains both copper and lead, and these impurities are removed either by the process described above or by evaporating the selenium to dryness with nitric acid and reducing the aqueous solution of selenious acid by means of sulphur dioxide (Nilson).

259 *Properties.*—Selenium, like sulphur, exists in several allotropic modifications (Berzelius, Hittorf), three well defined forms being known.[2]

1. Amorphous, vitreous, and colloidal selenium, soluble in carbon bisulphide. These three differ in appearance but may all be considered as belonging to the same allotropic form, and they are sometimes known as "liquid" selenium (Saunders).
2. Red crystalline selenium, which occurs in two distinct crystalline forms and is soluble in carbon bisulphide.
3. Metallic selenium, which is insoluble in carbon bisulphide.

Amorphous selenium is obtained as a finely divided brick-red powder, when a cold solution of selenious acid is precipitated by a current of sulphur dioxide. Other reducing agents, such as iron, zinc, stannous chloride, or phosphorous acid, also precipitate amorphous selenium from solutions of selenious acid, and it is also formed by the electrolysis of the acid. It has a specific gravity of 4·26, and is soluble in carbon bisulphide to the extent of 0·1 part in 100 of the solvent at 46·6°, dissolving also in benzene, and many other solvents.

Amorphous selenium is often obtained in a colloidal form which is soluble in water.[3] This colloidal selenium is formed when a solution of sulphur dioxide is added to a solution of selenious acid and when a dilute solution of the acid is reduced by hydrazine hydrate. It is a dark red powder

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[1] *Handbook of Inorganic Analysis* (1854), 154.

[2] Saunders, *Journ. Physical Chem.* 1900, **4**, 423, where a bibliography of this subject will be found.

[3] Schulze, *J. pr. Chem.* 1885, [2], **32**, 390; Gutbier, *Zeit. anorg. Chem.* 1902, **32**, 106.

which is completely soluble in water, forming a red fluorescent solution, but which gradually becomes insoluble on preservation. The solution may be boiled without undergoing any change, but the selenium is deposited on the addition of acids or salts. The solution on spontaneous evaporation deposits the selenium as a red transparent film.

Vitreous selenium is always produced when liquid selenium, which has been heated above 217°, is rapidly cooled. It then solidifies to a dark brownish-black glassy translucent amorphous brittle mass of vitreous selenium, which is also soluble in carbon bisulphide, and has a specific gravity of 4·28. These varieties have no definite melting point, softening gradually on heating.

Insoluble or metallic selenium is obtained by cooling melted selenium quickly to 210° and then keeping the melted mass at this temperature for some time. The selenium at length solidifies to a granular crystalline mass, the temperature rising suddenly in the act of solidification to 217°. This change from the amorphous to the metallic condition also takes place, only more slowly, at lower temperatures; thus, if a mass of amorphous or vitreous selenium be gradually heated, it softens and then, as soon as the temperature approaches 100°, begins to pass rapidly into the metallic form, the temperature rising to 217°. A similar change occurs at the ordinary temperature when amorphous selenium is placed in contact with quinoline, aniline and certain other liquids in which it is soluble.

If a concentrated solution of potassium or sodium selenide be exposed to the air, metallic selenium separates out in microscopic crystals, and it is also formed as a crystalline powder when sulphur dioxide is passed through a hot solution of selenious acid, the amorphous form, which is the first product, being rapidly converted into the metallic variety.

Metallic selenium melts at 217°, has the specific gravity 4·8 and sublimes in black hexagonal crystals, isomorphous with those of tellurium.[1] It can also be obtained in long leaf-like crystals from solution in quinoline.

When amorphous selenium is allowed to stand in contact with carbon bisulphide it is converted, rapidly in the light, more slowly in the dark, into red crystals. The same change is effected by many solvents, such as alcohol, benzene, chloroform, etc., whilst other solvents, such as quinoline, aniline,

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[1] Muthmann, *Zeit. Kryst.* 1890, **17**, 336.

selenium chloride, etc., convert it directly into the metallic form.[1]

The red crystalline form is slightly soluble in carbon bisulphide and can be obtained in two different modifications, both belonging to the monoclinic system. The form deposited from a hot solution consists of dark-red translucent crystals, which are isomorphous with the monoclinic form of sulphur.[2] Red crystalline selenium has the specific gravity 4·47 and, when it is heated, appears to melt at about 170–180°, but passes rapidly into the metallic form.

The change from amorphous or vitreous selenium into the metallic form is accompanied by an evolution of heat amounting to about 55 calories, and the change from the amorphous to the red crystalline form is also accompanied by evolution of heat, the exact amount of which is, however, not known.[3]

According to the experiments of Carnelley and Williams,[4] selenium boils at about 680°, and forms a dark-red vapour which condenses either in the form of scarlet *flowers of selenium*, or in dark shining drops of the melted substance. In a high vacuum it boils at 310°.[5] As in the case of sulphur, the vapour density of selenium diminishes very rapidly with the temperature; thus at 774° the vapour density[6] is 101·2 ($H=1$), at 815° it becomes 95·4 and at 900–950° it finally becomes constant at the value 78·6, corresponding with the formula Se_2, which it retains[7] up to 1800°. The molecular weight as determined from the freezing-point of solutions in phosphorus[8] corresponds nearly with the formula Se_8.

Metallic selenium conducts electricity, and exposure to light increases its conducting power.[9] The peculiar effect of light is best exhibited on selenium which has been exposed for a

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[1] Saunders, *Journ. Physical. Chem.* 1900, **4**, 423.

[2] Rammelsberg, *Ber.*, 1874, **7**, 669.

[3] Fabre, *Ann. Chem. Phys.* 1887 [6], **10**, 472; Petersen, *Zeit. physikal. Chem.*, 1891, **8**, 612.

[4] *Journ. Chem. Soc.* 1879, 563. See also Troost, *Compt. Rend.* 1882, **94**, 1508, and D. Berthelot, *Compt. Rend.* 1902, **134**, 75.

[5] Krafft, *Ber.* 1903, **36**, 1690, 4344.

[6] Szarvasy, *Ber.* 1897, **30**, 1244.

[7] Biltz, *Zeit. physikal. Chem.*, 1896, **19**, 415.

[8] Beckmann and Pfeiffer, *Zeit. physikal. Chem.* 1897, **22**, 609.

[9] Sale, *Proc. Roy. Soc.* 1873, **21**, 283; W. G. Adams, *Proc. Roy. Soc.* 1875, **23**, 535; W. Siemens, *Berlin, Ber. Akad.* 1875. S. Bidwell, *Phil. Mag.* 1885 [5], **20**, 1785. Marc, *Zeit. anorg. Chem.* 1903, **37**, 459; Pfund, *Phil. Mag.* 1904 [6], **7**, 26; Berndt, *Physikal. Zeitsch.* 1904, **5**, 121; Hopius, *Journ. Russ. Phys. Chem.* 1903, **35**, 581.

considerable time to a temperature of 210°, until it has attained a granular crystalline condition. When selenium in this condition is heated its electrical resistance is increased, whilst on exposing it to the action of diffused daylight, the electrical resistance instantly diminishes; this, however, is only a temporary change, for on cutting off the light, the electrical resistance of the selenium slowly increases, and after a short time reaches the amount exhibited before the exposure. This remarkable property of selenium may possibly be made use of for photometrical purposes.

When selenium is heated in the air it burns with a bright blue flame, forming selenious oxide and at the same time emitting a characteristic odour, resembling that of rotten horse-radish, the cause of which is unknown. The emission spectrum of selenium is seen when a small bead of the element is held in a non-luminous gas flame; it is a channelled spectrum highly characteristic and beautiful, consisting of a very large number of bright bands, which in the green and blue are arranged at regular intervals. The electric spark spectrum of selenium exhibits bright lines of which the most characteristic are seven in the green and three in the red.[1] According to Salet,[2] selenium, like sulphur, gives two emission spectra, one consisting of lines and the other of bands. The absorption spectrum of selenium has been examined by Gernez.[3]

The atomic weight of selenium has been determined by Pettersson and Ekman, who ascertained the composition of the oxide, SeO_2, and of silver selenite, Ag_2SeO_3, and obtained the number 78·5;[4] more recently Lenher[5] by the analysis of silver selenite and of ammonium selenibromide arrived at the number 78·7, whilst Meyer[6] by the electrolysis of silver selenite has obtained the number 78·6, which is now taken as the most probable value and agrees with the older determination of Berzelius,[7] derived from the analysis of the chloride.

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[1] W. M. Watts, *Spectrum Analysis*, 1904 (Longmans), p. 28.

[2] *Compt. Rend.* 1871, **73**, 559 and 742.

[3] *Ibid.* 1872, **74**, 1190.

[4] *Ber.* 1876, **9**, 1210.

[5] *Journ. Amer. Chem. Soc.* 1898, **20**, 555.

[6] *Ber.* 1902, **35**, 1591.

[7] *Pogg. Ann.* 1826, **8**, 21.

SELENIUM AND HYDROGEN.

HYDROGEN SELENIDE, SELENIURETTED HYDROGEN OR SELENIUM HYDRIDE. H_2Se.

260 This gas is formed when selenium vapour and hydrogen are heated together, and the amount which is thus produced is a function of the temperature. The quantity formed increases when the temperature is raised from 250° to about 575°, but above this point the amount appears gradually to diminish.[1]

Below 320° equilibrium is only very slowly established between selenium, hydrogen, and selenium hydride, but if the tube in which the experiment is carried out be coated internally with a layer of selenium, the condition of equilibrium is reached much more rapidly, the same final state being attained whether the gas originally placed in the tube is hydrogen or selenium hydride.[2]

When selenium is heated in a closed tube filled with hydrogen, it sublimes in the cool part of the tube in the form of beautiful glittering crystals, and these increase in number until the whole of the selenium has volatilised. The formation of these crystals depends upon the decomposition by heat of the seleniuretted hydrogen which is formed; for when selenium is heated in a tube filled with an indifferent gas, only red amorphous selenium is found to sublime.

Seleniuretted hydrogen is easily obtained by the action of dilute hydrochloric acid on potassium selenide, K_2Se, or on iron selenide, FeSe, which is prepared by adding selenium to heated iron, and it may be obtained pure and dry by acting on an excess of aluminium selenide, Al_2Se_3, over mercury with water.

$$Al_2Se_3 + 6H_2O = 2Al(OH)_3 + 3H_2Se.$$

It is also formed when organic materials such as colophonium are heated with selenium. It is a colourless, inflammable gas, possessing a smell which, to begin with, resembles that of sulphuretted hydrogen, but afterwards is found to have a much

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[1] Ditte, *Ann. de l'École norm. sup.* [1], **2**, 293; Pélabon, *Compt. Rend.* 1894, **118**, 142; 1894, **119**, 73; 1895, **121**, 401; 1897, **124**, 360.

[2] Bodenstein, *Zeit. physikal. Chem.* 1899, **29**, 429.

more persistent and intolerable odour, a small quantity affecting the mucous membrane in a remarkable degree, attacking the eyes, and producing inflammation and coughing which last for days.

Berzelius describes the effects as follows: [1]—"In order to become acquainted with the smell of this gas I allowed a bubble not larger than a pea to pass into my nostril; in consequence of its action I so completely lost my sense of smell for several hours that I could not distinguish the odour of strong ammonia, even when held under my nose. My sense of smell returned after the lapse of five or six hours, but severe irritation of the mucous membrane set in and lasted for a fortnight."

When exposed to light the gas slowly decomposes into its elements. The critical temperature of the gas is + 137°C., and its critical pressure 91 atmospheres; it condenses to a liquid which solidifies at −64°C., boils at −42°C. and has the specific gravity 2·12 at its boiling point. Its solubility in water is almost the same as that of the corresponding sulphur compound, 1 volume of water at 13°·2 dissolving 3·31 volumes of the gas.[2] The colourless solution reddens blue litmus paper, colours the skin a reddish-brown tint, and possesses the fœtid odour of the gas. Exposed to the air, the aqueous solution absorbs oxygen with the separation of red selenium. When added to solutions of salts of most of the heavy metals, it produces precipitates of the insoluble selenides in an analogous manner to sulphuretted hydrogen. Sulphur also decomposes it, forming sulphuretted hydrogen and precipitating selenium.

In order to ascertain the composition of seleniuretted hydrogen metallic tin is heated in a measured volume of the gas, when tin selenide is formed, and a volume of hydrogen is liberated equal to that of the original gas.

SELENIUM AND THE HALOGENS.

261 When the vapour of selenium is passed over melted fluoride of lead, a fluoride of selenium sublimes in crystals. These are soluble in hydrofluoric acid, and are decomposed by water (Knox). When selenium is exposed to gaseous fluorine it

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[1] Lehrbuch, 5 Aufl. **2**, 213.

[2] de Forcrand and Fonzes-Diacon, *Ann. Chim. Phys.* 1902, [7], **26**, 247.

fuses and finally takes fire, a white crystalline substance being formed. This is soluble in hydrofluoric acid, but is decomposed by water (Moissan).[1]

262 *Selenium Monochloride.* Se_2Cl_2. When a current of chlorine is passed over selenium, the latter melts and is converted into a brown oily liquid, which is selenium monochloride. It is more readily prepared by passing hydrochloric acid gas into a solution of selenium in fuming nitric acid.[2] Selenium monochloride is slowly decomposed by water according to the equation:

$$2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl,$$

and cannot be distilled without undergoing decomposition:

$$2Se_2Cl_2 = SeCl_4 + 3Se.$$

Selenium Tetrachloride. $SeCl_4$. This body is obtained by the further action of chlorine upon the monochloride, as well as when selenium dioxide is heated with phosphorus pentachloride (Michaelis); thus:—

$$3SeO_2 + 3PCl_5 = 3SeCl_4 + P_2O_5 + POCl_3.$$

The tetrachloride is a light yellow solid body, which on heating volatilises without previously melting, subliming in small crystals. It also crystallises from solution in phosphorus oxychloride in the form of bright shining cubes. It dissolves in water with formation of hydrochloric and selenious acids:

$$SeCl_4 + 3H_2O = 4HCl + H_2SeO_3.$$

When its vapour is heated its density, as determined by V. Meyer's method, diminishes, but the exact nature of the decomposition is not known.[3]

263 *Selenium Monobromide.* Se_2Br_2. Equal parts of bromine and selenium combine together with evolution of heat to form a black semi-opaque liquid, having a specific gravity at 15° of 3·6. It has a disagreeable smell resembling that of chloride of sulphur, and colours the skin a permanent red-brown tint. On heating it is decomposed, and when brought into contact with

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[1] *Ann. Chim. Phys.* 1891, [6], **24**, 239.

[2] Divers and Shimose, *Ber.* 1884, **17**, 866.

[3] Chabrié, *Bull. Soc. Chim.* 1889, [3], **2**, 803.

water, selenium, selenious acid and hydrobromic acid are formed; thus:—

$$2Se_2Br_2 + 3H_2O = 3Se + H_2SeO_3 + 4HBr.$$

Selenium Tetrabromide. $SeBr_4$. This compound is formed by the further action of bromine on the monobromide. It is an orange-yellow crystalline powder, best obtained by adding bromine to a solution of selenium monobromide in carbon bisulphide. It is very volatile, vaporising between 75° and 80° with partial decomposition and subliming in black six-sided scales. It possesses a disagreeable smell similar to that of chloride of sulphur, decomposes in contact with moist air into bromine and the monobromide, and dissolves in an excess of water with formation of hydrobromic and selenious acids.

Unstable double salts, such as K_2SeBr_6 and $(NH_4)_2SeBr_6$, are formed when selenious oxide is dissolved in hydrobromic acid and the alkali bromide then added.[1]

The *chlorobromides of selenium*, $SeCl_3Br$ and $SeClBr_3$, are orange-yellow crystalline substances (Evans and Ramsay).[2]

264 *Selenium Mono-iodide.* Se_2I_2. The compounds of selenium and iodine resemble those of selenium with chlorine and bromine. The mono-iodide is obtained when the two elements are brought together in the right proportions (Schneider), and forms a black shining crystalline mass, melting between 68° and 70° with the evolution of a small quantity of iodine. When more strongly heated, it decomposes into iodine, which volatilises, and selenium, which remains behind; and it is decomposed by water in a similar way to the corresponding bromide.

Selenium Tetra-iodide, SeI_4, is a granular dark crystalline mass, which melts at from 75° to 80° to a brownish-black liquid, translucent in thin films; when more strongly heated it decomposes into its elements.

SELENIUM AND OXYGEN.

Oxides and Oxy-acids of Selenium.

265 Only one oxide of selenium, the dioxide, SeO_2, is with certainty known to exist in the free state. A lower oxide is stated by Berzelius to be formed when selenium burns in the

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[1] Muthmann and Schäfer, *Ber.* 1893, **26**, 1008.

[2] *Journ. Chem. Soc.* 1884, 62.

air, and to be the cause of the peculiar smell then observed, which is so penetrating that if 1 mgrm. of selenium be burnt in a room the smell is perceptible in every part. This oxide, however, has not been isolated, and its existence is doubtful.[1]

Selenium also forms two oxy-acids—selenious acid, H_2SeO_3, and selenic acid, H_2SeO_4.

SELENIUM DIOXIDE. SeO_2.

266 When selenium is placed in a bent tube, as shown in Fig. 123, and strongly heated in a current of oxygen, contained in the gasholder and dried by passing over pumice stone saturated with sulphuric acid, it takes fire and burns with a bright blue flame, a white sublimate of solid selenium dioxide being deposited in the cool part of the tube. Thus obtained it forms long, four-sided, white, needle-shaped crystals, which do not melt when heated under the ordinary atmospheric pressure, but evaporate when heated to about 300°, yielding a

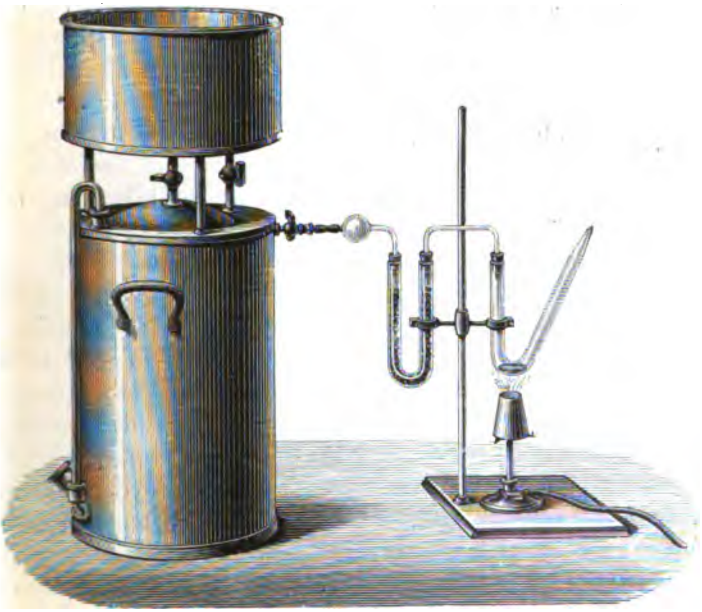

FIG. 123.

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[1] Peirce, *Amer. J. Sci.* 1896 (4), **2**, 163.

greenish-yellow-coloured vapour possessing a powerful acid smell (Berzelius).

It may also be prepared by dissolving selenium in nitric acid, evaporating several times with water, and finally heating and subliming in a current of oxygen.[1] It is decomposed by sulphur at the melting point of the latter, selenium and sulphur dioxide being produced.[2]

SELENIOUS ACID, H_2SeO_3.

267 Selenious acid is formed when selenium is heated with nitric acid, or when five parts of the dioxide are dissolved in one part of hot water. On cooling, clear, long, colourless, prismatic, nitre-shaped crystals of selenious acid separate out. These have a strong acid taste, and, when heated, decompose into selenium dioxide and water. If sulphur dioxide be allowed to pass into a hydrochloric acid solution of selenious acid, selenium is deposited as a red powder. This decomposition takes place but slowly in the cold and in absence of light; but when the liquid is heated, or exposed to sunlight, the change occurs quickly. Organic substances also bring about this reduction, and the colourless solution of the pure acid soon becomes tinged red when exposed to the air, owing to the presence of dust in the atmosphere. Selenious acid is distinguished from sulphurous acid by this reaction, for sulphurous acid gradually absorbs oxygen from the air. Selenious acid is also reduced to selenium by ferrous sulphate, hydriodic acid, hydrazine, hydroxylamine, and hypophosphorous acid, and is quantitatively converted into selenic acid by potassium permanganate. Selenium is also produced from the selenites by the action of certain moulds and bacteria, volatile odorous compounds being also produced by certain organisms.[3]

Selenious acid is a dibasic acid, and forms not only acid and normal salts, but also salts containing acid selenites united with selenious acid; thus, $HKSeO_3 + H_2SeO_3$.

The normal selenites of the alkali metals are easily soluble in water; those of the alkaline earth metals and the heavy metals

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[1] Divers and Haga, *Journ. Chem. Soc.* 1899, 537.

[2] Krafft and Steiner, *Ber.* 1901, **34**, 560.

[3] Maasen, *Journ. Chem. Soc.* 1902, ii. 629; Gosio, *Atti. R. Accad. Lincei*, 1904, [5], **13**, i. 642.

are insoluble; whilst all the acid salts are soluble compounds. When a selenite is heated on charcoal in the reducing flame, a characteristic horse-radish-like smell is emitted, said to be due to a selenide of carbon;[1] and when heated in a glass tube with sal-ammoniac, selenium sublimes. The selenites are further distinguished by the fact that red selenium is precipitated when sulphur dioxide is led into their solution in water or in hydrochloric acid. The salts are very poisonous.

268 *Selenyl Chloride, or Selenium Oxychloride.* $SeOCl_2$. This chloride of selenious acid is formed by the action of selenium dioxide on selenium tetrachloride (Weber):[2]

$$SeO_2 + SeCl_4 = 2SeOCl_2.$$

and when the oxide is heated with sodium chloride:[3]

$$2SeO_2 + 2NaCl = SeOCl_2 + Na_2SeO_3.$$

It is a yellow liquid which fumes on exposure to air, and which, when cooled below 10°, deposits crystals having a specific gravity of 2·44. It boils at 179°·5 (Michaelis), and decomposes with water in the same way as all acid chlorides. When mixed with thionyl chloride, selenium tetrachloride and sulphur dioxide are formed; thus:—

$$SeOCl_2 + SOCl_2 = SeCl_4 + SO_2.$$

Selenyl Bromide, $SeOBr_2$, is formed by the action of selenium tetrabromide on selenium dioxide. The two substances are melted together, and the compound, on cooling, crystallises in long needles.

SELENIC ACID. H_2SeO_4.

269 This acid, discovered in 1827 by Mitscherlich, is formed by the action of chlorine on selenium or on selenious acid in presence of water; thus:—

$$Se + 3Cl_2 + 4H_2O = H_2SeO_4 + 6HCl.$$

By the same reaction selenites may be converted into selenates, and bromine may for this purpose be employed instead of chlorine. Potassium selenate is also obtained when selenium

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[1] Rathke, *Ber.* 1903, **36**, 600.

[2] *Pogg. Ann.* 1859, **108**, 615.

[3] Cameron and Macallan, *Chem. News*, 1889, **59**, 267.

is fused with nitre and when a solution of a selenite is electrolysed.[1]

In order to prepare selenic acid, a solution of sodium selenite is treated with silver nitrate, and to the precipitate obtained, suspended in water, bromine is added (J. Thomsen); thus:—

$$Ag_2SeO_3 + H_2O + Br_2 = 2AgBr + H_2SeO_4.$$

It has also been obtained by the electrolysis of the copper salt[2] and by adding selenious acid to a solution of permanganic acid (prepared by adding sulphuric acid to barium permanganate), filtering from the precipitated oxide of manganese and evaporating.[3]

The aqueous solution of selenic acid can be concentrated by evaporation in the air, but it cannot be thus completely freed from water, as at a temperature of about 280° it begins to decompose into oxygen, selenium dioxide, and water. If heated in vacuo to 180° and then cooled, the whole solidifies to a crystalline mass consisting of the pure acid.[4] The acid crystallises in long hexagonal prisms, similar to those formed by sulphuric acid, and melts at 58°. It combines eagerly with water, forming a monohydrate which melts at 25°, and, like sulphuric acid, chars many organic substances. The specific gravity of the solid acid is 2·6273, whilst that of the liquid at 15° is 2·3557.

The concentrated solution of the acid is a colourless, very acid liquid, which is miscible with water in all proportions, heat being thereby evolved. The heated aqueous acid dissolves gold and copper with formation of selenious acid, whilst iron, zinc, and other metals dissolve with evolution of hydrogen and production of selenates. This acid is not reduced either by sulphur dioxide or by sulphuretted hydrogen, and differs in this respect, therefore, remarkably from selenious acid. When boiled with concentrated hydrochloric acid it decomposes with the evolution of chlorine and formation of selenious acid; thus:—

$$H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O.$$

This mixture dissolves gold and platinum, these metals combining with the chlorine thus set at liberty.

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[1] Müller, *Ber.* 1903, **36**, 4262.
[2] Metzner, *Compt. Rend.* 1898, **127**, 54.
[3] *Compt. Rend.* 1895, **123**, 236.
[4] Cameron and Macallan, *Chem. News*, 1889, **59**, 219.

Selenic acid is decomposed by sulphur at 55°, sulphuric acid being formed and selenium deposited, while a certain amount of selenious acid is also produced.[1]

The selenates exhibit the closest analogy with the sulphates so far as regards amount of water of crystallisation, crystalline form, and solubility. Barium selenate, like the sulphate, is completely insoluble in water, and is employed for this reason in the quantitative determination of selenic acid; it is, however, distinguished from barium sulphate inasmuch as when boiled with hydrochloric acid the insoluble selenate is decomposed into the soluble selenite, whereas barium sulphate remains unchanged. All the other selenates are also reduced to selenites by means of hydrochloric acid, and this reaction serves as a means of recognising these compounds.

SELENIUM AND SULPHUR.

270 Several substances have been at various times described as compounds of selenium and sulphur,[2] but they have all proved to be mixtures of the two elements,[3] which form several series of mixed crystals.[4]

SELENOSULPHUR TRIOXIDE. $SeSO_3$.

It has long been known that when selenium is dissolved in fuming sulphuric acid, a beautiful green colour is produced, and it has been proved that this is due to the formation of the above compound. This substance is best prepared by dissolving selenium in freshly distilled well-cooled sulphur trioxide. The compound then separates out in the form of tarry drops, which soon solidify to prismatic crystals having a dirty green colour and yielding a yellow powder when broken up. The compound dissolves in sulphuric acid with a green colour, and is decomposed on addition of water with

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[1] Krafft and Steiner, *Ber.* 1901, **34**, 562.

[2] Rathke, *J. pr. Chem.* 1870, **108**, 235; *Ber.* 1903, **36**, 594; Ditte, *Compt. Rend.* 1871, **73**, 625, 660; Gerichten, *Ber.* 1874, **7**, 26.

[3] Divers, *Chem. News*, 1885, **51**, 24; Bettendorf and von Rath, *Pogg. Ann.* 1870, **139**, 329.

[4] Ringer, *Zeit. anorg. Chem.* 1902, **32**, 183; Retgers, *Zeit. physikal. Chem.* 1893, **12**, 583.

separation of selenium and formation of sulphuric, sulphurous, and selenious acids. On heating, the body does not melt but decomposes into selenium, selenium dioxide, and sulphur dioxide (Weber).[1]

SELENOSULPHURIC ACID. $SO_2\begin{cases}OH\\SeH\end{cases}$.

This compound, which corresponds to thiosulphuric acid, was discovered by Cloez,[2] and, like this latter acid, is not known in the free state. Its potassium salt is obtained when a solution of sulphurous acid is mixed with one of potassium selenide, or, together with the salts of selenotrithionic acid, when selenium is dissolved in a solution of normal potassium sulphite.[3] The *selenosulphates* are isomorphous with the thiosulphates. and are decomposed by all acids, even by sulphurous acid, with the separation of red selenium.

SELENOTRITHIONIC ACID. $H_2SeS_2O_6$.

The potassium salt of this acid is formed when a solution of potassium selenosulphate is mixed with an excess of normal potassium sulphate and a concentrated solution of selenious acid; thus:—

$$SO_2\begin{cases}OK\\OK\end{cases}+SO_2\begin{cases}OK\\SeK\end{cases}+SeO\begin{cases}OH\\OH\end{cases}=$$

$$K_2S_2SeO_6+SeO\begin{cases}OK\\OK\end{cases}+H_2O.$$

The potassium salt forms monoclinic prisms and is stable in the air. According to Schulze,[4] the free acid is formed when selenious acid is treated with an excess of sulphur dioxide.

The same chemist has found that when selenious acid is kept in excess, an acid of the formula $H_2SSe_2O_6$ is obtained.

Sulphoselenoxytetrachloride, $ClSO_2(OSeCl_3)$, is obtained by the action of selenium tetrachloride upon chlorosulphonic acid as a mass of white crystals;[5] it melts at 165° and boils at 183°.

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[1] *Pogg. Ann.* 1875, **156**, 513.

[2] *Bull. Soc. Chim.* 1861, 112.

[3] Schaffgotsch, *Pogg. Ann.* 1853, **90**, 66; Rathke, *J. pr. Chem.* 1855, **95**, 1; Uelsmann, *Annalen*, 1860, **116**, 122.

[4] *J. pr. Chem.* 1885, [2], **32**, 405.

[5] Clausnizer, *Ber.* 1878, **11**, 2007.

TELLURIUM. $Te = 126{\cdot}6$ $(H = 1)$.
$= 127{\cdot}6$ $(O = 16)$.

271 Tellurium occurs in small quantities in the free state in nature, and was termed by early mineralogists *aurum paradoxum* or *metallum problematum*, in consequence of its metallic lustre. In 1782 native tellurium was more carefully examined by Müller von Reichenstein. He came to the conclusion that it contained a peculiar metal, and, at his suggestion, Klaproth[1] in 1798 made an investigation of the tellurium ores, confirming the views of the former experimenter that it contained a new metal, to which he gave the name of tellurium from *tellus*, the earth. Berzelius[2] in 1832 made a more exhaustive investigation of tellurium; he likewise considered the substance itself to be a metal, but its compounds were found to correspond so closely with those of sulphur and selenium, that tellurium was placed in the sulphur group.

Tellurium belongs to the rarer elements. It occurs in Transylvania, Hungary, California, Virginia, Colorado, Brazil, Bolivia, and Western Australia, in small quantities in the native state, but it is generally found in combination with metals, as graphic tellurium, or sylvanite $(AgAu)Te_2$; black or leaf tellurium, or nagyagite $(AuPb)_2$ $(TeSSb)_3$; silver telluride or hessite, Ag_2Te; tetradymite, or bismuth telluride, Bi_2Te_3, &c.; and also occurs in the red sulphur of Japan.

Preparation.—In order to prepare pure tellurium, tellurium-bismuth containing about 60 per cent. of bismuth, 36 per cent. of tellurium, and about 4 per cent. of sulphur is mixed with an equal weight of pure sodium carbonate, and the mixture then rubbed up with oil to a thick paste, and heated strongly in a well-closed crucible. The mass is then lixiviated with water, and the filtered solution, which contains sodium telluride and sodium sulphide, is exposed to the air, when the tellurium gradually separates out as a grey powder, which after washing and drying may be purified by distillation in a current of hydrogen (Berzelius).

On the large scale the alkaline residues from bismuth ores are treated with hydrochloric acid and then with sodium sulphite, which precipitates the tellurium.[3]

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[1] *Crell. Ann.* **1**, 91.

[2] *Pogg. Ann.* 1833, **28**, 392; 1834, **32**, 1 and 577.

[3] Matthey, *Proc. Roy. Soc.* 1901, **68**, 161.

In order to obtain the tellurium from graphic, or from black tellurium, the ore is treated with hydrochloric acid, to free it from antimony, arsenic, and other bodies. The residue is then boiled with aqua regia, and the filtrate evaporated to drive off the excess of nitric acid; ferrous sulphate is then added, which precipitates the gold, and the tellurium is thrown down in the filtrate by means of sulphur dioxide (v. Schrötter). The ores may also[1] be boiled with concentrated sulphuric acid, the solution diluted and then treated with hydrochloric acid, gold and silver thus being left behind and a clear solution obtained from which sulphur dioxide precipitates selenium and tellurium. When the crude material is again submitted to the same treatment a product containing 97—98 per cent. of tellurium is obtained.

The crude tellurium is best purified by treating it with aqua regia, expelling the excess of nitric acid by means of hydrochloric acid, and then diluting somewhat so that the tellurous acid remains in solution whilst the chloride of lead is precipitated. From the filtrate, the tellurium is precipitated by means of sulphurous acid. The material thus obtained, which may contain traces of selenium, lead, and other metals, is then fused in small portions with potassium cyanide, the mass extracted with water in the absence of air, and the tellurium thrown down from the clear filtrate by a current of air. It is finally melted and distilled in a current of hydrogen.[2]

Properties.—Tellurium is a silver-white body possessing a metallic lustre, and crystallising in rhombohedra; it is very brittle, and can therefore be easily powdered. Its specific gravity is 6·27 (Matthey): it melts at 452° (Carnelley and Williams), and boils at a still higher temperature, and may accordingly be easily purified by distillation in a stream of hydrogen gas. In an almost perfect vacuum it boils at 478°.[3]

Amorphous tellurium is obtained when a solution of tellurous or telluric acid is precipitated by means of sulphurous acid, hydrazine hydrate, hydroxylamine, and other reducing agents. It has the specific gravity 6·015, and when heated is converted with evolution of heat into the crystalline variety.[4] A colloidal solution of the element is often obtained when telluric acid is

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[1] Farbaky, *Zeit. angew. Chem.* 1897, 11.

[2] Brauner, *Monatsh.* 1889, **10**, 414.

[3] Krafft, *Ber.* 1903, **36**, 4344.

[4] Fabre and Berthelot, *Compt. Rend.* 1887, **104**, 1405.

reduced by reagents and a colloidal deposit when a solution in nitric acid is electrolysed.[1]

Tellurium burns with a blue flame when heated in the air, evolving white vapours of tellurium dioxide. It is insoluble in water and carbon bisulphide, but dissolves in cold fuming sulphuric acid, imparting to the solution a deep-red colour, which is probably due to the formation of a compound analogous to sulphur sesquioxide, namely, $STeO_3$, the tellurium being precipitated on the addition of water. On heating the sulphuric acid solution, the tellurium is oxidised and a sulphate is formed, sulphur dioxide being given off. In the same way it rapidly undergoes oxidation in the presence of nitric acid.

Hydrochloric acid does not attack tellurium, whilst caustic potash dissolves it with formation of potassium telluride and tellurite. When heated nearly to the melting-point of glass, tellurium emits a golden-yellow vapour, which gives an absorption spectrum, consisting of fine lines stretching from the yellow to the violet.[2] The emission spectrum of tellurium has been mapped by Salet[3] and Ditte,[4] the spark spectrum by Watts.[5]

According to Deville and Troost[6] the vapour of tellurium possesses a specific gravity of 9·0 at 1390°, and this remains unaltered at 1800°,[7] which number corresponds to a molecular weight of about 259. The molecule of tellurium therefore contains two atoms and has the formula Te_2.

272 *Atomic Weight of Tellurium.*—The determination of the atomic weight of tellurium is a problem of great interest. The earlier observers obtained the number 128, and this was confirmed in 1879 by Wills,[8] who analysed the double bromide of potassium and tellurium K_2TeBr_6, and converted the element into tellurous acid by means of nitric acid and of aqua regia. The close relation of tellurium to sulphur and selenium, however, rendered it highly probable, from considerations connected with the arrangement of the elements according to the periodic system (Vol. II. [1897], p. 59), that the atomic weight of tellurium would be found to be less than that of iodine (125·9).

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[1] Gutbier, *Zeit. anorg. Chem.* 1902, **32**, 51, 91; Gutbier and Resenscheck, *Zeit. anorg. Chem.* 1904, **40**, 264.

[2] Gernez, *Compt. Rend.* 1872, **74**, 1190.

[3] *Compt. Rend.* 1871, **73**, 559, 742.

[4] *Compt. Rend.* 1871, **73**, 262.

[5] *Spectrum Analysis*, p. 28.

[6] *Compt. Rend.* 1863, **56**, 871.

[7] Biltz, *Zeit. physikal. Chem.* 1894, **19**, 415.

[8] *Journ. Chem. Soc.* 1879, 704.

Brauner[1] then re-examined the question, but found that all reliable methods of determination (analysis of tellurous acid and of tellurium tetrabromide) led to about 126·5. He expressed the opinion that the substance known as tellurium contained some substance of higher atomic weight, and in this he believed himself to be confirmed by the fact that when the tellurium was previously sublimed in hydrogen its atomic weight was found by the analysis of the bromide to be considerably lower (126·5) than when it was fused in any indifferent gas (136·7).

More recent experiments have failed to confirm the existence of an impurity of high atomic weight in tellurium, although numerous investigations have been made on the subject, and tellurium from the most varied sources has been examined. Thus Staudenmaier,[2] who prepared tellurium dioxide from crystallised telluric acid and converted it into tellurium, obtained the number 126·6, and the same value resulted from the experiments of Chikashigé,[3] who employed the tellurium prepared from the red sulphur of Japan and analysed the tetrabromide. Metzner[4] prepared his tellurium by the decomposition of the hydride and obtained the value 126·9, whilst Pellini,[5] who separated his tellurium from the organic compound tellurium diphenyl, $Te(C_6H_5)_2$, arrived at the number 126·7.

Köthner,[6] by the analysis of the basic nitrate; Gutbier,[7] by the reduction of telluric acid and the dioxide with hydrazine, and A. Scott,[8] by the analysis of tellurium trimethyl iodide and bromide, all obtained figures ranging from 126·55–126·78.

The only result below 126 has been the value 125·4, obtained by Steiner,[9] who estimated the amount of carbon and hydrogen in tellurium diphenyl by combustion, and from this calculated the atomic weight of the tellurium, but this result has not been confirmed.

There seems, therefore, no doubt that the atomic weight of tellurium is greater than that of iodine, and its most probable value is at present taken as 126·6 (H = 1).

Radio-Tellurium.—Tellurium prepared from the pitchblende found in Joachimsthal is accompanied by a minute amount of a strongly radioactive substance, which is not precipitated

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[1] *Monatsh.* 1889, **10**, 411; *Journ. Chem. Soc.* 1889, 382.

[2] *Zeit. anorg. Chem.* 1895, **10**, 189.

[3] *Journ. Chem. Soc.* 1896, 881.

[4] *Compt. Rend.* 1898, **126**, 1716.

[5] *Ber.* 1901, **34**, 3807.

[6] *Annalen*, 1901, **319**, 1.

[7] *Ibid.* 1902, **320**, 52.

[8] *Proc. Chem. Soc.* 1902, 112.

[9] *Ber.* 1901, **34**, 570.

by hydrazine hydrochloride, but is precipitated by metallic bismuth. The nature of this substance is at present quite unknown.[1]

TELLURIUM AND HYDROGEN.

TELLURIUM HYDRIDE, OR TELLURETTED HYDROGEN. H_2Te.

273 This compound, discovered by Davy in 1810, is a colourless gas possessing a fœtid smell similar to that of sulphuretted hydrogen, and is not nearly so poisonous as seleniuretted hydrogen. It is formed in small quantities when tellurium is heated in hydrogen gas. If this is allowed to take place in a sealed tube, the same phenomenon presents itself as is observed with selenium, and the tellurium sublimes in long glittering prisms.

The gas is extremely unstable, and can only be prepared pure with great difficulty. It is formed, generally together with hydrogen, by the action of dilute acids on the tellurides of magnesium,[2] zinc, and aluminium,[3]

$$MgTe + 2HCl = MgCl_2 + TeH_2$$

It is also formed when 50 per cent. sulphuric acid is electrolysed at −15 to −20°, a piece of tellurium being used for the negative pole; the gas thus obtained when rapidly dried is almost pure.[4] It quickly decomposes into tellurium and hydrogen in the light, more slowly in the dark at the ordinary temperature, and is instantaneously decomposed by contact with moist air.

Tellurium hydride is easily combustible, burning with a blue flame. It is soluble in water, and this solution absorbs oxygen from the air, tellurium being deposited. Like sulphuretted hydrogen, telluretted hydrogen precipitates many of the metals from their solutions in the form of tellurides. The soluble tellurides, such as those of the alkali metals, form brownish-red solutions from which tellurium is deposited on exposure to the air.

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[1] Marckwald, *Ber.* 1903, **36**, 2662.

[2] Berthelot and Fabre, *Ann. Chim. Phys.* 1888, [6], **14**, 103.

[3] de Forcrand and Fonzes-Diacon, *Ann. Chim. Phys.* 1902, [7], **26**, 260.

[4] Ernyei, *Zeit. anorg. Chem.* 1900, **25**, 313.

The gas can readily be condensed to a colourless liquid which boils at 0° and freezes to a colourless mass melting at about −48°. The density of the gas was found by Ernyei to be about 65·1 ($H=1$), and its volume is not altered when it is completely decomposed by being heated with metallic zinc or tin, so that its molecular formula is H_2Te.

TELLURIUM AND THE HALOGENS.

274 *Tellurium Tetrafluoride,* TeF_4, is prepared by heating the dioxide with hydrofluoric acid in a platinum retort. It distils over as a colourless, transparent, very deliquescent mass.

When a solution of tellurous acid in hydrofluoric acid is concentrated, crystals of the formula TeF_4+4H_2O separate out. Powdered tellurium becomes incandescent on exposure to fluorine gas, the tetrafluoride being formed.[1]

Tellurium Dichloride. $TeCl_2$.—This compound is formed together with the tetrachloride when chlorine is passed over melted tellurium. It may be separated from the less volatile tetrachloride by distillation; and thus obtained it forms an indistinctly crystalline, almost black mass which gives a greenish-yellow powder, melts at 175°, boils at 327°,[2] and yields a deep red-coloured vapour having the density 6·89.[3]

Water decomposes the compound with separation of tellurium and formation of tellurous acid; thus:—

$$2TeCl_2+3H_2O=Te+H_2TeO_3+4HCl.$$

Tellurium Tetrachloride, $TeCl_4$, is formed by the further action of chlorine on the preceding compound, and is also formed when tellurium is treated with sulphur monochloride.[4] It is a white crystalline body and melts at 224°,[5] forming a yellow liquid, which when more strongly heated becomes at last of a dark red colour and boils at 380°,[6] without decomposition. It is extremely hygroscopic and is decomposed when

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[1] Moissan, *Ann. Chim. Phys.* 1891, [6], **24**, 239.

[2] Carnelley and Williams, *Journ. Chem. Soc.* 1879, 563; 1880, 125.

[3] Michaelis, *Ber.* 1887, **20**, 2488.

[4] Lenher, *J. Amer. Chem. Soc.* 1902, **24**, 188.

[5] Carnelley and Williams, *Journ. Chem. Soc.* 1880, 125.

[6] Michaelis, *Ber.* 1887, **20**, 2491.

thrown into cold water, an insoluble oxychloride being formed together with tellurous acid. Hot water, on the other hand, gives rise only to the formation of the latter compound. Like the corresponding tetrachlorides of sulphur and selenium, it forms crystalline compounds with a large number of metallic chlorides, and also unites with hydrogen chloride.[1] The vapour density of the tetrachloride is 9·2 (Michaelis).

Tellurium Dibromide, $TeBr_2$, is best obtained by heating the tetrabromide with tellurium. On heating it volatilises in the form of a violet vapour, which condenses to black needles, melting at 280°, and again solidifying to a crystalline mass; it boils at 339°.

Tellurium Tetrabromide, $TeBr_4$.—In order to prepare this compound, finely divided tellurium is added to bromine which has been cooled down to 0°. It is a dark yellow solid body which can be sublimed without decomposition at about 300° *in vacuo*, and then forms fiery red crystalline crusts.[2] It dissolves in a small quantity of water with a yellow colour, but when added to a large quantity of water the solution becomes colourless from the formation of hydrobromic and tellurous acids. It boils at 420°, and decomposes into the dibromide and bromine. It forms double salts with the bromides of the alkali metals, and unites with hydrogen bromide.

Tellurium Tetraiodide, TeI_4.—Tellurium and iodine can be melted together in all proportions without forming a compound,[3] the substance formerly described as tellurium di-iodide being a mixture.

Tellurium tetraiodide is produced by the action of hydriodic acid on tellurous acid:

$$H_2TeO_3 + 4HI = TeI_4 + 3H_2O.$$

It forms an iron-grey crystalline mass which melts when gently heated, and when heated more strongly decomposes with separation of iodine. It is but slightly soluble in cold water, and is decomposed by boiling water. It forms double salts with the alkali iodides, corresponding with the double bromides and chlorides,[4] and also unites with hydrogen iodide.

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[1] Metzner, *Compt. Rend.* 1897, **125**, 23.

[2] Brauner, *Journ. Chem. Soc.* 1889, 396.

[3] Gutbier and Flury, *Zeit. anorg. Chem.* 1902, **32**, 108.

[4] Wheeler, *Zeit. anorg. Chem.* 1893, **3**, 428.

TELLURIUM AND OXYGEN.

OXIDES AND OXY-ACIDS OF TELLURIUM.

275 Three oxides of tellurium are known, TeO, TeO_2 and TeO_3 as well as the acids, H_2TeO_3, and H_2TeO_4 corresponding to the last two of these.

TELLURIUM MONOXIDE. TeO.

276 This substance is left behind as a brownish-black amorphous mass when tellurium sulphoxide, $TeSO_3$, is heated to 230° *in vacuo*, sulphur dioxide being evolved. On heating in the air or on exposure to moist air it is gradually oxidised. Sulphuric acid forms with it a red solution, from which a crystalline mass of *tellurium sulphate*, $Te(SO_4)_2$, soon separates. The monoxide when heated in hydrochloric acid gas is converted into tellurium dichloride.[1]

TELLURIUM DIOXIDE. TeO_2.

277 This oxide occurs in the impure state in nature as tellurite or tellurium ochre, at Facebay in Transylvania. It is formed by the combustion of tellurium in the air, and separates out in small octahedra when tellurium is dissolved in warm nitric acid. It is only very slightly soluble in water, and the solution does not redden blue litmus paper. On heating it melts to a lemon-yellow liquid which boils on further heating without decomposition, whilst on cooling it solidifies to a white crystalline mass. Although this is an acid-forming oxide, it also exhibits basic properties, inasmuch as it reacts with certain acids such as sulphuric and nitric acids, forming an unstable class of salts which are decomposed by water. The basic nitrate on ignition leaves a residue of TeO_2,[2] which can in this way be obtained pure.[3]

TELLUROUS ACID. H_2TeO_3.

278 Is obtained by pouring a solution of tellurium in dilute nitric acid into water. It separates out in the form of a very

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[1] Divers and Shimose, *Ber.* 1883, **16**, 1004; *Journ. Chem. Soc.* 1883, 319.

[2] Klein, *Ann. Chim. Phys.* 1887, [6], **10**, 108.

[3] Norris and Fay, *Amer. Chem. J.* 1898, **20**, 278.

voluminous precipitate, which when placed over sulphuric acid dries to a light white powder. It is but slightly soluble in water, and the solution possesses a bitter taste. Tellurous acid, like sulphurous acid, is dibasic, and therefore forms two series of salts; thus we have normal potassium tellurite, K_2TeO_3, and acid potassium tellurite, $KHTeO_3$. Other more complicated series of salts exist, such as:—$K_2Te_2O_5$, $K_2Te_4O_9$, $K_2Te_6O_{13}$. The tellurites of the alkali metals are soluble in water, and are formed by the solution of the acid in an alkali, or by fusing the dioxide with an alkali. The tellurites of the alkaline earth metals are only slightly soluble, and those of the other metals are insoluble in water, but soluble in hydrochloric acid.

Tellurous acid is converted into telluric acid by the action of potassium permanganate both in acid and alkaline solution. The amount of tellurous acid in a solution may be estimated in this manner.[1]

Potassium tellurite is reduced by many micro-organisms, violet or dark coloured solutions being produced.[2]

TELLURIUM TRIOXIDE. TeO_3.

279 This oxide is prepared by heating crystallised telluric acid to nearly a red heat. If it is heated too strongly, a small quantity of dioxide is formed with evolution of oxygen, but this can be separated by treatment with hydrochloric acid, in which it dissolves whilst the trioxide is insoluble. Tellurium trioxide is an orange-yellow crystalline mass, which, when strongly heated, decomposes into oxygen and the dioxide.

TELLURIC ACID. $H_2TeO_4 + 2H_2O$ or H_6TeO_6.

When tellurium or the dioxide is fused with potassium carbonate and saltpetre, potassium tellurate is formed; thus:—

$$Te_2 + K_2CO_3 + 2KNO_3 = 2K_2TeO_4 + N_2 + CO.$$

The same salt is produced when chlorine is passed through an alkaline solution of a tellurite; thus:—

$$K_2TeO_3 + 2KOH + Cl_2 = K_2TeO_4 + 2KCl + H_2O.$$

On dissolving the fused mass in water, and adding a solution of

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[1] Brauner, *Monatsh.* 1891, **12**, 29.

[2] Gosio, *Atti. R. Accad. Lincei*, 1904, [5], **13**, i. 422.

barium chloride, the insoluble barium tellurate is precipitated: this is purified by washing with water, and afterwards decomposed by the exact amount of sulphuric acid necessary, the clear acid solution, filtered from the sulphate of barium, being evaporated.

It may also be obtained by dissolving the dioxide in caustic potash in presence of hydrogen peroxide,[1] but is best prepared pure by dissolving tellurium in nitric acid, in presence of chromic acid, and evaporating. The crystalline mass is then purified by being washed with nitric acid, dissolved in water, precipitated by nitric acid, again dissolved in water, and the solution finally evaporated.[2]

The acid crystallises at the ordinary temperature in prisms of the composition $H_2TeO_4 + 2H_2O$, and is dimorphous,[3] but at temperatures below 10° crystals of the composition $H_2TeO_4 + 6H_2O$ are deposited from solution. The formula of the ordinary form of the acid in solution as determined by the freezing point method is, however, H_6TeO_6, that of the second hydrate being, therefore, $H_6TeO_6 + 4H_2O$. When the crystals are heated to 160°, they lose water, and a different modification of telluric acid, known as *allo-telluric acid*, remains as a white powder, which dissolves very slowly in cold water, but readily in hot water, forming a solution which deposits the original hydrated acid. When the ordinary acid, H_6TeO_6, is heated in a sealed tube to 140°, it melts and produces a solution of allo-telluric acid, which then slowly passes back to the original form. The allo-acid is a much stronger acid than telluric acid and also differs from it by yielding precipitates with sodium carbonate and with albumin solution. It appears to have the formula $(H_2TeO_4)_n$ and to stand to telluric acid in much the same relation as metaphosphoric acid, $(HPO_3)_n$, does to orthophosphoric acid, H_3PO_4. Several intermediate compounds seem also to exist, the exact relations between which have not been ascertained.[4]

Telluric acid is readily reduced with formation of free tellurium by sulphur dioxide, hydrazine hydrate, alkaline solutions of hydroxylamine, sulphuretted hydrogen, hypophosphorous acid and other reducing agents.

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[1] Gutbier and Wagenknecht, *Zeit. anorg. Chem.* 1904, **40**, 260.

[2] Staudenmaier, *Zeit. anorg. Chem.* 1895, **10**, 189.

[3] Gossner, *Zeit. Kryst.* 1904, **38**, 498.

[4] Mylius, *Ber.* 1901, **34**, 2208; see also Brauner, *Journ. Chem. Soc.* 1895, 549; and Gutbier, *Zeit. anorg. Chem.* 1902, **32**, 96.

The Tellurates.—Amongst the tellurates only those of the alkali-metals are more or less readily soluble in water, those of the remaining metals being either sparingly soluble or insoluble in water, although generally dissolving readily in hydrochloric acid.

Certain of the tellurates are found to exist in two modifications, viz.:—

(*a*) As colourless salts, soluble in water or in acids.
(*b*) As yellow salts, insoluble in water and in acids.

Besides these modifications we are acquainted not only with normal and acid tellurates, but with several other series of acid salts. Normal potassium tellurate, $K_2TeO_4 + 5H_2O$, is obtained upon evaporation of a solution, either in the form of crystalline crusts, or as a gum-like residue, both being soluble in water. A salt containing $2H_2O$ has also been obtained.

The more complex salts, $K_2TeO_4.TeO_3.4H_2O$ and

$$K_2TeO_4.3TeO_3.4H_2O,$$

are also known, and are termed di- and tetra-tellurates. Salts of the type $Na_4TeO_5 + 8H_2O$ have also been prepared (Mylius), and the existence of these affords additional evidence that the formula of the acid is not simply H_2TeO_4.

Barium tellurate, $BaTeO_4 + 3H_2O$, is a white powder, not precipitated in dilute solutions as it is not quite insoluble in water. The di- and tetra-tellurate of barium, as well as calcium and strontium tellurates, are similar white precipitates, whilst magnesium tellurate is rather more soluble. All the other tellurates are insoluble in water.

When a tellurate is heated to redness, oxygen is evolved and a tellurite formed, and this reduction also occurs, with the evolution of chlorine, when a tellurate is heated with hydrochloric acid, thus:—

$$K_2TeO_4 + 2HCl = K_2TeO_3 + H_2O + Cl_2.$$

280 *Tellurium Oxychloride.* $TeOCl_2$.—This substance[1] is obtained by heating the compound of tellurium dioxide with hydrochloric acid, $TeO_2 + 2HCl$, above 90°,

$$TeO_2, 2HCl = TeOCl_2 + H_2O.$$

On further heating, it decomposes into the tetrachloride and the dioxide,

$$2TeOCl_2 = TeCl_4 + TeO_2.$$

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[1] Ditte, *Compt. Rend.* 1876, **83**, 336, 446.

Tellurium Oxybromide. $TeOBr_2$.—This compound is obtained in a similar manner to the oxychloride and is a faintly yellow coloured mass (Ditte).

TELLURIUM AND SULPHUR.

281 A disulphide, TeS_2, and a trisulphide, TeS_3, were described by Berzelius as formed by the action of sulphuretted hydrogen upon solutions containing an alkali tellurite and telluric acid respectively. Both of these compounds yield up nearly all their sulphur to carbon bisulphide and are therefore probably mixtures.[1] Solutions which probably contain these compounds in the colloidal form are, however, formed in the early stages of the precipitation.[2]

Salts of the formula $3K_2S, TeS_2$ (potassium thio-tellurite) and K_2TeS_4 (thio-tellurate) are, however, known.

TELLURIUM SULPHOXIDE. $TeSO_3$.

This compound is obtained by the direct union of tellurium with sulphur trioxide.[3] It is a red amorphous, transparent solid, which softens at 30°. On heating for some time at 35°, it becomes of a light reddish-brown colour. Water decomposes it with formation of tellurium and sulphuric acid, along with other products. On heating to 230°, it loses sulphur dioxide and forms tellurium monoxide.

NITROGEN. N = 13·93. (H=1)
= 14·04. (O=16)

282 Dr. Rutherford, Professor of Botany in the University of Edinburgh, showed in the year 1772 that when animals breathe in a closed volume of air, it not only becomes laden with impure air from the respiration, but contains, in addition, a constituent which is incapable of supporting combustion and respiration. He prepared this constituent by treating air in which animals

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[1] Becker, *Annalen*, 1876, **180**, 257; Brauner, *Journ. Chem. Soc.* 1895, 545.

[2] Gutbier, *Zeit. anorg. Chem.* 1902, **32**, 272, 292.

[3] Weber, *J. pr. Chem.* 1882, [2], **25**, 218; Divers and Shimose, *Ber.* 1883, **16**, 1009.

had breathed with caustic potash, by means of which the fixed air (carbonic acid) can be removed. The residual air was found to extinguish a burning candle, and did not support the life of animals which were brought into it.[1]

In the same year Priestley found that when carbon is burnt in a closed bell-jar over water, one-fifth of the common air is converted into fixed air which can be absorbed by milk of lime; a residual (phlogisticated) air incapable of supporting either combustion or respiration being left. Priestley, however, did not consider that this air was a constituent of the atmosphere, and it is to Scheele that we owe the first statement, contained in his treatise on *Air and Fire*, that the "air must be composed of two different kinds of elastic fluids." The constituent known as mephitic or phlogisticated air was first considered to be a simple body by Lavoisier, who gave to this gas the name azote (from *α*, privative, and *ζωή*, life, by which it is still usually designated in France). Chaptal first suggested the name nitrogen, which it now generally bears (from *νίτρον*, saltpetre, and *γεννάω*, I give rise to), because it is contained in saltpetre.

The gas left after the removal of the oxygen from purified air was regarded as nitrogen until 1894, when it was found by Ramsay and Rayleigh[2] that this contained 1·186 per cent. of other gases, which could not, like nitrogen, be made to combine with oxygen or with heated magnesium (see Argon). The admixed gas was subsequently found to contain the members of the helium group of gases.

Nitrogen is found in the free state in the atmosphere, of which it forms about four-fifths by bulk, and occurs also in combination in many bodies such as ammonia, in the nitrates, and in many organic substances which form an essential part of the bodies of vegetables and animals.

283 *Preparation.*—Pure nitrogen cannot readily be prepared from air, as its separation from the gases of the helium group can only be effected by bringing the whole of the nitrogen into the combined state. It can, however, be obtained from nitrogen compounds in a variety of ways.

(1) When a concentrated solution of ammonium nitrite is heated, the following reaction takes place:

$$NH_4NO_2 = N_2 + 2H_2O.$$

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[1] Rutherford, *De aere Mephitico. Edinb.* 1772.

[2] *Phil. Trans.* 1895, **186**, 187.

It is more convenient to employ a mixture of sodium nitrite with ammonium sulphate, which by double decomposition yields sodium sulphate and ammonium nitrite, the latter then decomposing into nitrogen and water. The addition of a little potassium bichromate prevents the formation of any nitric oxide, and the best results are obtained with a solution of 1 part of sodium nitrite, 1–2 parts of ammonium sulphate, and 1 part of potassium bichromate, the gas being then washed through dilute sulphuric acid.[1]

(2) Pure nitrogen is also formed by the action of chlorine upon ammonia; thus:—

$$8NH_3+3Cl_2=N_2+6NH_4Cl.$$

The chlorine evolved in a large flask passes into a three-necked Woulffe's bottle containing a strong aqueous solution of ammonia. The nitrogen gas which is here liberated is collected in the ordinary way over water, as shown in Fig. 124. Care must, however, be taken in this preparation that the ammonia is always present in excess, otherwise chloride of nitrogen may be formed, and this is a highly dangerous body, which explodes most violently (p. 516).

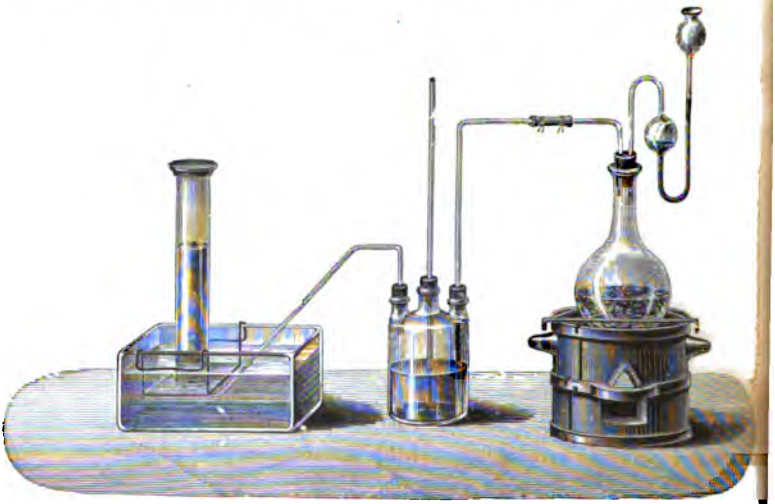

FIG. 124.

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[1] Knorre, *Chem. Ind.* 1902, **25**, 531. See also Veley, *Journ. Chem. Soc.* 1903, 736; Sorensen, *Zeit. anorg. Chem.* 1894, **7**, 38; Berger, *Bull. Soc. Chim.* 1904, [3], **31**, 662.

(3) By adding a solution of ammonia or an ammonium salt to an alkaline solution of sodium hypobromite:

$$2NH_3+3NaOBr=3NaBr+3H_2O+N_2.$$

The nitrogen is then washed successively through dilute sulphuric acid and dilute caustic soda solution and, if required perfectly pure, passed over heated copper and copper oxide.[1]

Urea, CON_2H_4, may also be decomposed by alkaline sodium hypobromite,

$$CON_2H_4+3NaOBr+2NaHO=3NaBr+Na_2CO_3+N_2+3H_2O,$$

but the nitrogen thus produced always contains nitrous oxide.[2]

(4) By passing a mixture of ammonia with oxygen through a heated tube containing metallic copper or iron. The hydrogen of the ammonia is oxidised to water and the excess of oxygen and any oxides of nitrogen which may be formed are removed by the heated metal:

$$4NH_3+3O_2=2N_2+6H_2O.$$

(5) When nitrous oxide or nitric oxide is passed over heated copper or iron the gas is decomposed and free nitrogen is produced:

$$N_2O+Cu=CuO+N_2.$$

Nitrogen is also evolved in many other reactions and decompositions, such as the action of sulphuric acid on a mixture of ammonium nitrate and glycerol[3] and the decomposition by heat of ammonium bichromate.

284 The oxygen of the air can readily be removed, yielding the mixture of gases formerly known as atmospheric nitrogen. This can be done in a variety of ways:—

(1) A small light porcelain basin is allowed to swim on the water of a pneumatic trough, a small piece of phosphorus brought into the basin and ignited, and the basin then covered by a large tubulated bell-jar (see Fig. 125). The phosphorus burns with the deposition of a white cloud of phosphorus pentoxide, which, however, soon dissolves, whilst on cooling, one-fifth of the contents of the bell-jar is found to be filled with water. The colourless residual gas is nitrogen; this may

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[1] Baly and Donnan, *Journ. Chem. Soc.* 1902, 908.

[2] Rayleigh, *Proc. Roy. Soc.* 1898, **64**, 95.

[3] Mai, *Ber.* 1901, **34**, 3805.

be easily proved by first equalising the level of the water inside and outside the bell-jar, after which, on opening the stopper and plunging a burning taper into the bell-jar, the flame is seen to be instantly extinguished. The nitrogen thus obtained is never perfectly pure, as, in addition to elements of the helium group, it always contains small quantities of oxygen which have not been removed by the combustion of the phosphorus. In presence of aqueous vapour, phosphorus slowly absorbs the oxygen of the air, at temperatures above 15°, whilst the sulphides of the alkali metals as well as moist sulphide of iron (obtained by heating flowers of sulphur with iron filings) act in a similar way.

FIG. 125.

(2) Air contained in a gas-holder is allowed to pass through tubes, T and T′, Fig. 126, containing caustic potash and sulphuric acid for the purpose of purifying the air from carbon dioxide and drying it. The air thus purified is passed over turnings of pure metallic copper contained in a long glass tube (e f) which is heated to redness in a charcoal- or gas-furnace; copper oxide is thus formed, and atmospheric nitrogen passes over and is collected in the pneumatic trough.

(3) Copper also rapidly absorbs oxygen from the air at the ordinary temperature in presence of a solution of ammonia, the oxide which is formed being dissolved by the ammonia; in order to obtain nitrogen by this method a slow current of air is passed through a tall cylinder containing copper turnings over which a solution of ammonia is allowed to drop continuously. The oxygen is absorbed and the resulting nitrogen, after washing with dilute sulphuric acid to remove traces of

ammonia, is collected in the usual manner. The last traces of oxygen are best removed by a solution of chromous chloride, $CrCl_2$, and this method, when carried out with other precautions, yields a gas quite free from oxygen or oxides of nitrogen.[1]

285 *Properties.*—Pure nitrogen is a colourless, tasteless, inodorous gas, which is distinguished by its inactive properties; hence it is somewhat difficult to ascertain its presence in small quantities. As has been said, it does not support combustion, nor does it burn nor render lime-water turbid. It combines directly with but very few non-metals, although indirectly it can easily be made to form compounds with most of these elements, and many of its compounds, such as nitric acid, ammonia, chloride of nitrogen, &c., possess characteristic and remarkable properties. It combines directly with a number of the metals, such as lithium, calcium, barium, and magnesium, yielding compounds termed *nitrides.* The specific gravity of nitrogen is 0·96717 (air = 1) and the weight of 1 litre is 1·2508 gram (Leduc),[2] while according to Rayleigh[3] the weight of a litre is 1·25107, and the density compared with air is 0·96737. The density of "atmospheric" nitrogen, on the other hand, is 0·97209, and one litre at 0°, and under the normal pressure, weighs 1·25718 grm. (Rayleigh).

FIG. 126.

Nitrogen was first liquefied by Cailletet by compressing it

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[1] Threlfall, *Phil. Mag.* 1893, [5], **35**, 1.

[2] *Compt. Rend.* 1896, **123**, 805; 1898, **126**, 413.

[3] *Proc. Roy. Soc.* 1893, **53**, 134; 1894, **55**, 340.

to 200 atmospheres and allowing it suddenly to expand. It was then obtained in much larger quantities by Wroblewski[1] and Olszewski,[2] and can now be prepared in any quantity (p. 108). It forms a colourless liquid, which boils under atmospheric pressure at −195·5° and has the critical temperature −149°, the critical pressure 27·54 atmospheres, and the critical volume 42·6 c.c. If allowed to evaporate in a vacuum the temperature falls considerably and the nitrogen solidifies, forming a colourless, crystalline mass, which melts at −210·5°. The specific gravity of the liquid at the boiling point is 0·8103 (Baly and Donnan[3]), 0·8042 (Dewar[4]), and that of the solid at −252·5° is 1·0265.

Nitrogen is but slightly soluble in water, one volume of water absorbing only 0·02348 of the gas at 4°, and a smaller quantity at higher temperatures.[5] The coefficient of the solubility of nitrogen (c) from 0–20° may be found by the following interpolation formula:—

$$c = 0{\cdot}023481 - 0{\cdot}0005799t + 0{\cdot}00000885t^2.$$

The gas is rather more soluble in alcohol than in water.

There are two characteristic spectra of nitrogen, both obtained by passing the spark from an induction coil through a Geissler's tube containing a small quantity of highly rarefied nitrogen gas. The nitrogen spectrum commonly obtained in this way is a channelled one, exhibiting a large number of bright bands especially numerous in the violet. If the spark is produced by high tension, as when a Leyden jar is used, a spectrum of numerous fine lines distributed throughout the length of the spectrum is obtained (Plücker).

Under ordinary conditions nitrogen is incombustible, but a mixture of nitrogen and oxygen can be made to ignite under certain circumstances. Thus if a powerful current of electricity be passed through the primary of a large induction coil, an arching flame is seen to issue from each secondary pole, provided these are not too far apart, the two flames joining in the centre; the flame is due to the combination of the nitrogen and oxygen of the air to form oxides of nitrogen.

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[1] *Compt. Rend.* 1883, **97**, 1553; 1884, **98**, 982; 1886, **102**, 1010; *Monatsh.* 1885, **6**, 204.

[2] *Compt. Rend.* 1884, **99**, 133; 1885, **100**, 350.

[3] Baly and Donnan, *Journ. Chem. Soc.* 1902, 912. See also Ramsay and Drugman, *Journ. Chem. Soc.* 1900, 1228.

[4] *Proc. Roy. Soc.* 1904, **73**, 251.

[5] Winkler, *Ber.* 1891, **24**, 3605.

When the flame has once been formed the distance between the secondary poles may be considerably increased without extinguishing the flame, and the latter may then be blown out and re-ignited by a taper. The flame does not extend to the surrounding air because heat is absorbed in the combination, and this can therefore only occur when energy is supplied to the mixture from an external source.[1]

286 *Assimilation of Free Nitrogen by Plants.*—As already mentioned, nitrogen forms an essential constituent of a very large number of animal and vegetable substances and is necessary for the maintenance of animal and vegetable life. It was however for a long time believed that members of the vegetable kingdom were unable to take up the free nitrogen of the air, and that they were dependent for their supply of this element on combined nitrogen contained in the atmosphere and in the soil chiefly in the form of nitric acid and ammonia. About the year 1886 it was shown that certain leguminous plants, such as the white lupine, when grown in air free from ammonia and other nitrogen compounds, contain more nitrogen than was originally present in the seed and in the soil in which they were sown, and they must, therefore, have obtained the excess from the nitrogen of the air; since then it has been shown that certain algæ, fungi, and mosses behave in a similar manner, and it is not improbable that further investigation will show that this property is possessed by many other kinds of plants. This assimilation by plants is brought about by the action of certain micro-organisms, termed bacteroids, which are found in nodules on the roots, and absorb the free nitrogen from the air, forming compounds of nitrogen which are then assimilated by the plant.[2] Other classes of micro-organisms also play a considerable part in the assimilation of nitrogen by plants, as many of the latter are incapable of directly assimilating ammonia, although they can take up nitric acid; the micro-organisms in the soil bring about the conversion of ammonia into nitric acid, one species of these converting the former into nitrous acid, and another converting the nitrous into nitric acid.[3]

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[1] Spottiswoode, *Proc. Roy. Soc.* 1881, **31**, 173; Crookes, *Chem. News*, 1892, **65**, 302. See also Rayleigh, *Journ. Chem. Soc.* 1897, 181; Muthmann and Hofer, *Ber.* 1904, **36**, 438.

[2] For further details see Lawes and Gilbert, *Phil. Trans.* 1890, 180 (B) 1; *Journ. Roy. Agric. Soc.* 1891, 657; *Proc. Roy. Soc.* 1890, **46**, 85; Schloesing, *Compt. Rend.* 1891, **113**, 776; Marshall Ward, *Nature*, 1893-4, **49**, 511.

[3] Warrington, *Journ. Chem. Soc.* 1891, 484.

287 *The atomic weight of nitrogen* was determined by Stas, who converted silver into silver nitrate, and also ascertained the equivalent of ammonium chloride to silver, and to silver nitrate. These experiments led to the numbers 13·93 (H = 1), 14·04 (O = 16), and these are still employed. It has, however, been pointed out by several observers that this atomic weight is decidedly higher than would be expected from the density of the gas, which, after being corrected for deviation from the gas laws, leads to the number 13·900 (Leduc),[1] 13·904 (Rayleigh).[2] Some recent determinations have given lower numbers[3] than those of Stas, but further investigation of the subject is required.

NITROGEN AND HYDROGEN.

AMMONIA. $NH_3 = 16·93$.

288 Ammonia is found in the atmosphere forming a small but essential constituent of the air. It likewise occurs in combination with nitric and nitrous acids in rain-water, and especially as sal-ammoniac, NH_4Cl, and as ammonium sulphate, $(NH_4)_2SO_4$, deposited on the sides, the craters, and in the crevices of the lava streams of active volcanoes, as well as mixed with boric acid in the fumaroles of Tuscany. Many samples of rock-salt also contain traces of ammoniacal compounds, and all fertile soil contains this substance, which is likewise found, although in small quantities, widely distributed in rain and in running water, as well as in sea-water, in clays, marls, and ochres. Ammoniacal salts are also found in the juices of plants and in most animal fluids, especially in the urine.

Ammonia was known to the early alchemists in the form of the carbonate under the name of *spiritus salis urinæ*. In the fifteenth century it was known that the same body may be obtained by the action of an alkali upon sal-ammoniac; and Glauber, in consequence, termed this body *spiritus volatilis*

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[1] *Compt. Rend.* 1807, **125**, 299; See also D. Berthelot, *Compt. Rend.* 1898, **126**, 1030; and Vèzes, *Compt. Rend.* 1898, **126**, 1714.

[2] Rayleigh, *Proc. Roy. Soc.* 1897, **62**, 209; 1904, **73**, 153.

[3] Hibbs, *J. Amer. Chem. Soc.* 1896, **18**, 1044; Dean, *Journ. Chem. Soc.* 1900, 117; Scott, *Journ. Chem. Soc.* 1901, 147; Guye, *Compt. Rend.* 1904, **138**, 1213; Guye and Bogdan, *Compt. Rend.* 1904, **138**, 1494; Jaquerod and Bogdan, *Compt. Rend.*, 1904, **139**, 49.

salis armoniaci. Sal-ammoniac, which was known to the Latin Geber, appears to have been brought in the seventh century from Asia to Europe, and was known under the name of *sal-armoniacum.* It is possible that this sal-ammoniac was derived from the volcanoes of Central Asia. Geber, however, describes the artificial production of the salt by heating urine and common salt together. In later times, sal-ammoniac was brought into Europe from Egypt, where it was prepared from the soot obtained by burning camel's dung. Its original name was altered to *sal-armoniacum*, and then again changed to *sal-ammoniacum.* This last name served originally among the Alexandrian alchemists to describe the common salt (chloride of sodium) and native sodium carbonate, which were found in the Libyan desert in the neighbourhood of the ruins of the temple of Jupiter Ammon. Boyle says in his "Memoirs for the Natural History of Human Blood :"[1]—"Though the *sal-armoniac* that is made in the East may consist in great part of camel's urine, yet that which is made in Europe, and commonly sold in our shops, is made of man's urine." Later on, sal-ammoniac was obtained by the dry distillation of animal refuse, such as hoofs, bones, and horns ; the carbonate of ammonia thus obtained being neutralised with hydrochloric acid. From this mode of preparation ammonia was formerly termed *spirits of hartshorn.*

Up to the time of Priestley, ammonia was known only in the state of aqueous solution, termed spirits of hartshorn, or *spiritus volatilis salis ammoniaci.* Stephen Hales, in 1727, observed that when sal-ammoniac is heated with lime in a vessel closed by water, no air is given out, but, on the contrary, water is drawn into the apparatus ; Priestley, in 1774, repeated this experiment, with the difference, however, that he used mercury to close his apparatus. He thus discovered ammonia gas, to which he gave the name of *alkaline air.* He also found that, when electric sparks are allowed to pass through this alkaline air, its volume undergoes a remarkable change, and the residual air is found to be combustible. Berthollet, following up this discovery in 1785, showed that the increase of volume which ammonia gas thus undergoes is due to the fact that it is decomposed by the electric spark into hydrogen and nitrogen. This discovery was confirmed, and the composition of the gas more accurately determined by Austin (1788), H. Davy (1800), and Henry (1809). It was shown by them

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[1] Boyle, op. 4, 597.

that, in the reaction above described, two volumes of ammonia are resolved into three volumes of hydrogen and one of nitrogen.

289 It has been shown, first by Deville,[1] then by Donkin, that ammonia can be synthetically prepared by the direct combination of its elements,[2] the electric discharge being, for this purpose, passed through a mixture of nitrogen and hydrogen. This action was formerly attributed to the silent discharge, but it has been shown that sparks are necessary.[3]

If a mixture of 3 vols. of hydrogen and 1 vol. of nitrogen be subjected to the action of the electric discharge in a eudiometer, containing above the mercury a little dilute sulphuric acid, the whole volume finally disappears, the two gases slowly combining to form ammonia, which dissolves in the acid as fast as it is formed. It is likewise obtained together with nitrous acid by passing nitrogen over a mixture of platinum black and alkali.[4]

Ammonia is also formed :—

(1) By the putrefaction or decay of the nitrogenous constituents of plants and animals.

(2) By the dry distillation of the same bodies; that is, by heating these substances strongly out of contact with air.

(3) By the reduction of the salts of nitric or nitrous acid.

It is to the first of these processes that we owe the existence of ammonia in the atmosphere, whilst the second serves for the production of ammonia and its compounds on the large scale.

At the present day almost all the ammonium salts are prepared from the ammoniacal liquor which is obtained as a by-product in industries where coal is carbonised, such as the manufacture of coal-gas and coke, as also from the blast-furnace gases, and from the gas made from coal by the Mond-process. Coal consists of the remains of an ancient vegetable world, and contains from 0·8 to 2·4 per cent. of nitrogen, some of which, in the process of the dry distillation of the coal, is obtained in the form of ammonia dissolved in the water and other products formed at the same time.

This liquor, which contains very little, if any, free ammonia, but chiefly the sulphide, carbonate, sulphite, and thiosulphate of ammonia, is then boiled, sometimes with milk of lime, to liberate

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[1] *Leçons*, 64.
[2] W. F. Donkin, *Proc. Roy. Soc.* 1873, **21**, 281.
[3] Dixon, *Manch. Lit. and Phil. Soc.* 1888, [4], **1**, 91.
[4] Loew, *Ber.* 1890, **23**, 1443.

the whole of the ammonia, sometimes without this addition, in which case only the ammonia present as sulphide and carbonate is recovered. This ammonia distils over and is collected in sulphuric acid, somewhat diluted with water, with which it combines, ammonium sulphate being formed as follows:—

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

This salt crystallises out without evaporation when a sufficient concentration is reached, and is removed by means of perforated ladles, and may be further purified by recrystallisation. This substance serves for the preparation of most of the ammoniacal compounds. If sal-ammoniac is to be prepared the distillate is collected in hydrochloric acid, or liquid hydrochloric acid is run into the aqueous ammonia obtained by distillation of the gas liquor (p. 500), and the solution is then evaporated to dryness and the salt purified by sublimation.

290 *Preparation.*—If any one of these ammoniacal salts be heated with an alkali, such as potash or soda, or with an alkaline earth, such as lime, the ammonia is set free as gas. In order to prepare the gas it is only necessary, therefore, to heat together sal-ammoniac and slaked lime; thus:—

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

In order to ensure the decomposition of all the sal-ammoniac, a large excess of lime is usually employed. One part by weight of powdered sal-ammoniac is for this purpose mixed with two parts of caustic lime slaked to a fine dry powder; these are well mixed together, and then introduced into a capacious flask, placed on a piece of wire gauze and heated by a Bunsen-lamp. The ammonia gas, which comes off when the mixture is gently heated, is then dried by allowing it to pass through a cylinder filled with small lumps of quicklime, or by placing a layer of the latter over the mixture of ammonium chloride and slaked lime in the flask, and the gas thus dried may be collected either over mercury, or, like hydrogen, by upward displacement in an inverted dry cylinder as shown in Fig. 127, inasmuch as the gas is lighter than air.

Gaseous ammonia may be very conveniently prepared for laboratory use by gently warming strong commercial aqueous ammonia or by allowing the strong solution to drop from a tap funnel on to lumps of caustic soda placed in a cylindrical glass vessel or flask furnished with a delivery tube, by which means a regular and continuous evolution of the gas is obtained.

291 *Properties.*—Pure ammonia is a colourless gas, possessing, like its aqueous solution, a peculiar pungent alkaline odour and caustic taste. In the solid state, however, it possesses but a very faint smell. Ammonia gas turns red litmus-paper blue, like the alkalis, neutralises acids, and forms with them a series of stable compounds, termed the *ammonium salts.* It is a very stable compound, but gradually decomposes into its constituents when heated,[1] the decomposition being practically complete at 1000°. The density of the gas is 0·5971 (Leduc).

FIG. 127.

Ammonia is not combustible, and a flame is extinguished if plunged into the gas. If, however, ammonia be mixed with oxygen, the escaping gas may be ignited, and burns with a pale yellow flame, with formation of water, nitrogen gas, and nitric acid, HNO_3. Another method of showing the combustibility of ammonia is to put a jet of this gas into the air holes of an ordinary Bunsen-burner, in which a flame of coal-gas is already burning; the flame becomes at once coloured yellow, and increases greatly in dimensions. A third experiment of this nature

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[1] Crafts, *Compt. Rend.* 1880, **90**, 309; Perman and Atkinson, *Proc. Roy. Soc.* 1904, **74**, 110.

is, to allow a stream of oxygen gas to bubble through a small quantity of strong aqueous ammonia placed in a flask and warmed as shown in Fig. 128; on bringing a light in contact with the mixed gases issuing from the neck of the flask they will be seen to burn with a large yellow flame.

Ammonia gas was first liquefied by Faraday, in 1823, by heating a compound of silver chloride with ammonia, $AgCl{\cdot}2NH_3$, placed in one limb of a strong hermetically sealed bent tube whilst the other limb was placed in a freezing mixture. Liquid ammonia is also easily obtained by leading the gas into a tube plunged in a freezing mixture composed of crystallised calcium chloride and ice, and having a temperature of $-40°$, and forms a colourless highly refracting liquid, boiling at $-38{\cdot}5°$, and freezing at $-77{\cdot}05°$ [1] to a mass of white translucent crystals of solid ammonia (Faraday). The critical temperature is 131° and the critical pressure 113 atmospheres.[2] The vapour pressure of the liquid is 4·19 atmospheres at 0°, 8·40 at 20°, and 20 at 50° (Pictet).

Fig. 128.

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[1] Ladenburg and Krügel, *Ber.* 1899, **32**, 1828.

[2] Vincent and Chappuis, *Journ. de Phys.* 1886, [2], **5**, 58.

Liquid ammonia is, like water, a bad conductor of electricity, its specific conductivity being $1{\cdot}33 \times 10^{-7}$ at $-79°$. It dissolves a large number of substances, many of which undergo electrolytic dissociation.

The co-efficient of expansion of liquid ammonia is 0·00204, and, therefore, larger than that of most liquids having a higher boiling point; its specific gravity compared with water at 0° is 0·6234.[1]

Ammonia is largely used for the artificial production of ice. For this purpose an apparatus (Fig. 129) was invented by M. Carré in which no force-pump was required. It consists of two strong iron vessels connected by a vent-pipe of the same metal. The cylinder (A) contains water saturated with ammonia gas at 0°. When it is desired to procure ice, the vessel (A) containing the ammonia solution, which we may term the retort, is gradually heated over a large gas-burner. The ammonia gas is thus driven out of solution, and as soon as the pressure in the interior of the vessel exceeds that of seven atmospheres, it condenses in the double-walled receiver (B). When the greater portion of the gas has thus been driven out of the water, the apparatus is reversed, the retort (A) being cooled in a stream of cold water, whilst the liquid which it is desired to freeze is placed in a cylinder which fits into the interior portion of the hollow cylinder. A reabsorption of the ammonia by the water now takes place, and a consequent evaporation of the liquefied ammonia in the receiver. This evaporation is accompanied by the absorption of heat which becomes latent in the gas. Thus the receiver is soon cooled down far below the freezing point, and the liquid contained in the vessel is frozen. For ice-

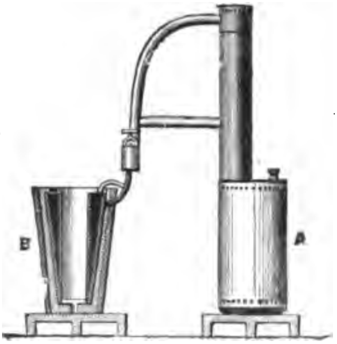

FIG. 129.

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[1] Joly, *Annalen*, 1861, **117**, 181.

making by ammonia on a large scale condensation is effected by compressing the ammonia in metal tubes cooled by water; the liquid then circulates through a series of tubes placed in contact with the material or air space which is to be cooled, and in these it evaporates, thus producing a considerable fall of temperature, and the gas passes back to the pump to be again compressed as before. The tubes are frequently placed in brine, which is thereby strongly cooled and is then either circulated through pipes placed in the water to be frozen or employed for cooling a current of air.

292 Ammonia gas is very soluble in water, one gram of water absorbing at 0° and under normal pressure 0·875 grms. or 1148 cc. of the gas. The solubility at different temperatures and under a pressure of 760 mm. of mercury is given in the following table (Roscoe and Dittmar):[1]—

Temp.	Gram.	Temp.	Gram.	Temp.	Gram.	Temp.	Gram.
0°	0·875	16°	0·582	32°	0·382	48°	0·244
2°	0·833	18°	0·554	34°	0·362	50°	0·229
4°	0·792	20°	0·526	36°	0·343	52°	0·214
6°	0·751	22°	0·499	38°	0·324	54°	0·200
8°	0·713	24°	0·474	40°	0·307	56°	0·186
10°	0·679	26°	0·449	42°	0·290		
12°	0·645	28°	0·426	44°	0·275		
14°	0·612	30°	0·403	46°	0·259		

The same observers have found that the absorption of ammonia in water does not follow the law of Dalton and Henry at the ordinary atmospheric temperature, inasmuch as the quantity absorbed does not vary directly as the pressure. Solutions of the gas, containing 2·5–22·5 $^{\circ}/_{\circ}$, moreover, do not follow the law below 60°, the partial pressure of the ammonia in the vapour increasing more rapidly than the amount dissolved when the concentration is varied at constant temperatures.[2] Sims[3] has shown that at higher temperatures the deviations from the law become less until at 100° the gas follows the law, the quantity absorbed being directly proportional to the pressure, taken of course under pressures higher than the ordinary

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[1] *Journ. Chem. Soc.* 1860, 128.

[2] Perman, *Journ. Chem. Soc.* 1903, 1168; compare Konowaloff, *J. Russ. Chem. Soc.* 1899, **31**, 910.

[3] *Journ. Chem. Soc.* 1862, 17.

atmospheric pressure, inasmuch as boiling water does not dissolve any of the gas under the pressure of one atmosphere.

In order to show the great solubility of ammonia gas in water the same apparatus may be employed which was used for exhibiting the solubility of hydrochloric acid in water (Fig. 49, p. 198), the lower balloon being filled with water slightly coloured with red litmus solution.

The liquor ammoniæ of the shops, a solution of the gas in water, is prepared by passing the gas, which has been previously washed, into a flask containing water kept cool by being placed in a large vessel of cold water, considerable heat being evolved in the condensation of the gas (Fig. 52, p. 201).

The commercial liquor ammoniæ is now frequently prepared directly from the ammoniacal liquor of the gas-works instead of from sal-ammoniac. For this purpose the liquor is heated, together with milk of lime, in a still similar to that employed in manufacturing ammonium sulphate (p. 495). The gas which is evolved is first passed through a system of cooling tubes, then through several scrubbers containing milk of lime, and finally through a series of tubes filled with charcoal, by means of which any remaining empyreumatic impurities are removed. By this method a pure gas can be obtained which is absorbed in water.

The following table gives the percentage of ammonia contained in aqueous solutions of different specific gravity (Carius):—

Specific Gravity.	Per Cent. NH_3.
0·8844	36·0
0·8864	35·0
0·8976	30·0
0·9106	25·0
0·9251	20·0
0·9414	15·0
0·9593	10·0
0·9790	5·0

The fact that great heat is evolved in the production of the saturated solution of ammonia is rendered evident by the following experiment. If a rapid current of air be passed through a cold concentrated solution of ammonia, the gas will be driven out of solution, and an amount of heat will be absorbed exactly equal to that which was given off when the solution of the gas was made, in consequence of which the temperature of the liquid will be seen to fall below −40°. A small quantity of mercury may thus be frozen. Ammonia is very soluble in alcohol, 1 litre of the solution saturated at 0° containing 130 grams of ammonia, and this solution is frequently used in the laboratory.

293 *Composition of Ammonia.*—In order to determine the composition of ammonia the arrangement shown in Fig. 130 is employed. The ammonia gas is placed in the closed limb of the syphon eudiometer, after which the mercurial column in both limbs is brought to the same height, the volume accurately read off, and a series of electric sparks from the induction coil allowed to pass through the gas until its volume undergoes no further alteration. The tube and gas are next allowed to cool, and the pressure in both limbs again adjusted. On the volume being again measured it is seen to have doubled. Oxygen is next added in such proportion that the mixture shall contain no more than 35 per cent. of the explosive mixture of oxygen and hydrogen (2 volumes of hydrogen to 1 of oxygen), and an electric spark is passed through the mixture. From the alteration of volume which takes place, the proportion of hydrogen to nitrogen can readily be deduced, as is seen from the following example:—

Volume of ammonia	20·0
„ nitrogen and hydrogen . . .	40·0
After the addition of oxygen	157·5
After the explosion	112·5

Hence 45 volumes have disappeared, of which 30 consisted of hydrogen; consequently two volumes of ammonia have yielded on decomposition three volumes of hydrogen and one volume of nitrogen.

That the relation between the hydrogen and nitrogen which combine to form ammonia gas is that of three volumes of the former to one of the latter can be shown by the following experiment due to Hofmann:[1]—

A glass tube (Fig. 131), 1 to 1·5 metre long, sealed at one end and having a small stoppered portion separated from the rest of the tube by a glass stopcock, is filled with chlorine at the

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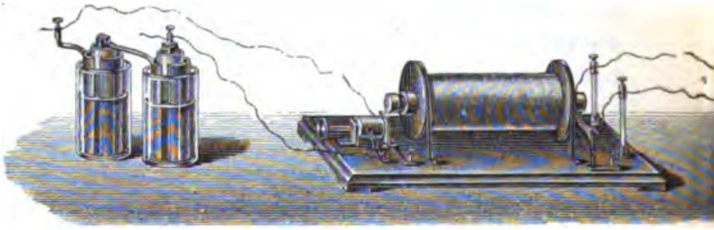
[1] *Introduction to Modern Chemistry.*

pneumatic trough over warm water. After the tube has been allowed to drain for some time, the stopcock is turned and the closed portion containing the chlorine is marked off into three equal portions by means of indiarubber rings. Strong ammonia is then poured into the open end of the tube and allowed to fall drop by drop through the stopcock into the chlorine, a small lambent yellowish-green flame marking the entrance of each drop. The addition of ammonia is continued until the whole of the chlorine present is supplied with hydrogen at the expense of the ammonia, and the white deposit of ammonium chloride is then dissolved by shaking up the liquid within the tube. Dilute sulphuric acid is then added to combine with the excess of ammonia, and finally the pressure within the tube is made equal to the atmospheric pressure by means of a syphon tube dipping under water, as shown in Fig. 132.

"Both temperature and pressure being now at the mean, all the requisite conditions are fulfilled for obtaining an exact knowledge of the true volume of nitrogen; and this, on inspection, is found exactly to fill one of the three divisions marked off at the outset on our tube. Now, bearing in mind that we started with the three divisions full of chlorine, and that we have saturated this chlorine with hydrogen supplied by the ammonia; bearing in mind, moreover, that hydrogen combines with chlorine, bulk for bulk, it is evident that the one measure of nitrogen which remains in the tube has resulted from the decomposition of a quantity of ammonia containing three measures of hydrogen. It is, therefore, clearly proved by this experiment that ammonia is formed by the union of three volumes of hydrogen with one volume of nitrogen" (Hofmann). The reaction which occurs between ammonia and chlorine in this experiment is not a simple removal of the hydrogen by



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chlorine, since nitrogen chloride is produced as an intermediate product and is subsequently decomposed.[1]

Another method of demonstrating the same fact is by the electrolysis of a strong solution of ammonia. For this purpose, the solution, mixed with a little ammonium sulphate to increase its conductivity, is introduced into a Hofmann apparatus (Fig. 74, p. 274), and subjected to the action of a moderately strong current of electricity; hydrogen is evolved at the negative pole and nitrogen at the positive pole, the volume of the former being three times as large as that of the latter.

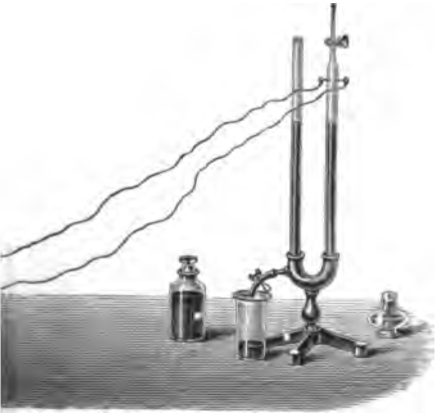

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FIG. 131.

294 *Detection and Estimation of Ammonia.*—The method adopted for the detection and estimation of small traces of ammonia with Nessler's reagent has already been described under Natural Waters (see p. 324). If the quantity of ammonia or of ammonium salt be larger, it may be detected by the peculiar smell of the gas, by its alkaline reaction, and by the formation of white fumes in presence of strong hydrochloric acid. These fumes consist of ammonium chloride, NH_4Cl, and are formed by the direct combination of the ammonia and hydrogen chloride:—

$$NH_3 + HCl = NH_4Cl.$$

When an ammoniacal salt is present, the ammonia must be liberated by heating the solid salt, or its solution, with a caustic

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[1] Noyes and Lyon, *J. Amer. Chem. Soc.* 1901, **22**, 460.

alkali. For the estimation of ammonia in quantities larger than those for which Nessler's method is applicable, it is usual to distil the ammonia, either into hydrochloric or sulphuric acid of known strength, and then to ascertain, by volumetric analysis with a standard solution of alkali, the amount of acid remaining free, or into hydrochloric acid of unknown strength to which a solution of chloroplatinic acid, H_2PtCl_6, is added. On evaporating the resulting solution to dryness on a water-bath, and exhausting with alcohol, an insoluble yellow precipitate of ammonium platinichloride, $(NH_4)_2PtCl_6$, is left, and this can either be collected on a weighed filter, or it may be ignited and the quantity of the metallic platinum remaining weighed, from which the weight of ammonia is calculated.

FIG. 132.

In addition to its use in the laboratory and as a means of obtaining artificial cold, ammonia is also largely employed for the preparation of alum, sodium carbonate, aniline colours, and in the manufacture of indigo.[1]

295 *Combination of Ammonia with Acids.*—Mention has been frequently made in the foregoing pages of the combination which takes place between ammonia and acids. This takes place very readily when gaseous ammonia is brought into contact with gaseous hydrogen chloride, and may be illustrated by inverting a jar containing hydrogen chloride over one of ammonia, dense white fumes of ammonium chloride being at once produced. The presence of moisture is, however, necessary for this combination to take place, and when the gases have been carefully dried by long exposure to pure phosphorus pentoxide no combination occurs.[2] Thus ammonia unites with hydrochloric acid to form the compound NH_3,HCl or NH_4Cl, and with hydrobromic acid to form NH_3,HBr or NH_4Br, whilst with sulphuric acid it yields $2NH_3,H_2SO_4$ or $(NH_4)_2SO_4$. In a similar manner ammonia combines with almost all other acids yielding compounds containing the group of atoms NH_4. Thus the compound NH_4Cl may be regarded as hydrochloric acid, HCl, in which the hydrogen atom has been replaced by the group NH_4, just as potassium chloride is hydrochloric acid in which the hydrogen atom is replaced by a potassium atom. The two substances do, in fact, bear a strong resemblance to each other both in their chemical and physical properties, and all the other substances obtained by the combination of ammonia with acids are similarly related to the salts of potassium. An aqueous solution of ammonia, moreover, acts in many ways as though it contained a base similar in character to the metallic hydroxides, and it is therefore supposed that a small amount of ammonium hydroxide, $NH_4.OH$, is present in aqueous ammonia, although the compound has not yet been isolated.

The group of atoms NH_4 is therefore a never-varying constituent in a series of compounds, and behaves in these compounds as though it were a simple substance: to such a group the name of "*compound radical*" is given, and as in this case the group in combination has the same effect on the properties of the substance as a metal, it is termed *ammonium*, the compounds with acids being known as the *ammonium salts*,

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[1] On the Manufacture of Liquor Ammoniæ, see Lunge's work on *Coal-Tar and Ammonia* (London, Gurney and Jackson, 1900).

[2] Baker, *Journ. Chem. Soc.* 1894, 674; 1898, 422; see also Gutmann, *Annalen*, 1898, **299**, 3.

as they correspond to the salts of potassium, sodium, &c. They are described together with these in Vol. II. (1897), p. 284.

HYDRAZINE OR DIAMIDE, N_2H_4.

296 This compound was first obtained by Curtius in 1887 by the action of hot dilute acids on triazo-acetic acid, a substance described in Vol. III., Part II. (2nd edition), p. 107, which was supposed by him to have the composition $C_3H_3N_6(COOH)_3$, and to contain the group $-N=N-$ three times.[1] It has since been obtained from other organic compounds containing two nitrogen atoms combined together; among these may be mentioned amidoguanidine, which has the constitution $NH_2.C(NH).NH.NH_2$. As this substance is obtained without difficulty from ammonium thiocyanate, it affords the best means for the preparation of hydrazine in quantity, and a description of the preparation may be therefore shortly given here, although the intermediate compounds will not be described till later.

Ammonium thiocyanate, NH_4CNS, is heated for some time at a constant temperature of 170 – 180°, and the residue, which consists chiefly of guanidine thiocyanate, treated first with strong sulphuric acid, then with a little fuming sulphuric acid; the mixture, after cooling, is mixed with nitric acid of sp. gr. 1·5, and the whole poured into water. Crude nitro-guanidine, $NH_2.C(NH).NH.NO_2$, separates out, and is at once treated with zinc dust and just sufficient dilute acetic acid for its reduction. The solution obtained by the reduction of 208 grams of nitroguanidine is then evaporated to 1200 c.c., mixed with a solution of 260 grams of caustic soda in 500 c.c. of water, and boiled for 8—10 hours. The cooled liquid is poured off from the sodium hydrogen carbonate which separates out, and mixed with 260 c.c. of concentrated sulphuric acid; the greater part of the hydrazine separates out as the sulphate, which is quite pure after a single recrystallisation.[2]

Hydrazine is also formed in small amount by the reduction of potassium nitrososulphate, $KON:N.O.SO_3K$, with sodium amalgam in the cold,[3] and by the action of sodium bisulphite,

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[1] Curtius, *Ber.* 1887, **20**, 1632; Hantzsch and Silberrad, *Ber.* 1900, **33**, 58.

[2] Thiele, *Annalen*, 1892, **270**, 1.

[3] Duden, *Ber.* 1894, **27**, 3498; Divers and Haga, *Journ. Chem. Soc.* 1896, 1610.

followed by that of zinc dust and acetic acid, on an aqueous solution of hyponitrous acid.[1]

Free hydrazine is difficult to prepare on account of the great stability of the hydrate, which is formed whenever the base is liberated in presence of water. It was first isolated in 1895 by Lobry de Bruyn,[2] who treated the hydrochloride with sodium methoxide in presence of methyl alcohol;

$$N_2H_5Cl+NaOCH_3=N_2H_4+NaCl+CH_3.OH.$$

It is, however, best prepared[3] by gradually adding the hydrate to anhydrous barium oxide, heating for some time at 110—120° and then distilling under 150—100 mm. pressure, the air of the apparatus being displaced by hydrogen so as to prevent the oxidation of the base. The distillate is not quite free from water and must therefore be again distilled over baryta. The free base is a colourless liquid, which boils at 113·5° and readily solidifies forming crystals which melt at 1·4°. It has the critical temperature 380° and the specific gravity 1·014 at 15°/15°. The base is extraordinarily hygroscopic and mixes readily with water or alcohol, but is only very sparingly soluble in organic solvents generally. It fumes in the air and is readily inflammable, but not explosive. It acts as a most violent reducing agent, and bursts into flame when brought into contact with chlorine, free nitrogen and hydrochloric acid being formed; on bromine and iodine it also reacts vigorously, forming the corresponding acids. It slowly oxidises in the air and when strongly heated decomposes, the final products being ammonia and nitrogen,

$$3N_2H_4=N_2+4NH_3.$$

Free hydrazine dissolves many salts and yields solutions which conduct electricity, so that its action in this respect is comparable with that of water and ammonia.

297 *Hydrazine Hydrate*, N_2H_4,H_2O, may be obtained by distilling hydrazine sulphate with a solution of caustic potash in a silver retort, connected without rubber or cork to a silver condensing tube; the distillation is continued till the last drop has passed over, and the distillate subjected to fractional distillation, by which the hydrazine hydrate is readily separated

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[1] Brackel, *Ber.* 1900, **33**, 2115; Erdmann, *Lehrbuch.*

[2] *Rec. Trav. Chim.* 1894, **13**, 433.

[3] Lobry de Bruyn, *Rec. Trav. Chim.* 1895, **14**, 85; 1896, **15**, 174.

from the excess of water. It can also be prepared[1] by decomposing the bromide with alcoholic potash and distilling at the pressure of 121—125 mm., under which the hydrate passes over at 73° ; at this temperature the vapour does not attack glass, so that a silver retort is unnecessary.

Hydrazine hydrate forms a strongly refractive almost odourless caustic-tasting liquid, which fumes strongly in the air, but may be kept unaltered in closed vessels although the dilute solution decomposes on preservation; it has a sp. gr. of 1·0305 at 21°,[2] and solidifies in a mixture of solid carbonic acid and ether, but melts again below $-40°$. It boils at 118·5° under 739·5 mm. pressure, but the vapour is partially dissociated into free hydrazine and water, which recombine on cooling. At 138° under the ordinary pressure this decomposition is complete, and at higher temperatures decomposition into nitrogen, ammonia, and water occurs.[3] In aqueous solution a determination of the molecular weight gave numbers corresponding to the formula $N_2H_4.2H_2O$.

Hydrazine hydrate when hot attacks glass strongly, and also quickly destroys cork and indiarubber; it is a very strong poison for lower organisms.[4] It is the most powerful reducing agent known, quickly precipitating all the more easily reducible metals from their solutions even in the cold. It also at once converts the halogens and sulphur into their hydrogen compounds. The hydrate decomposes in the presence of platinum black with formation of nitrogen, hydrogen, and ammonia.[5]

It is a very strong base, and like ammonia unites with acids to form well-defined salts, most of which are readily soluble in water. Unlike ammonia, however, it forms more than one series of salts, giving with hydrochloric acid, for example, two salts, $N_2H_4.HCl$ and $N_2H_4.2HCl$, and with hydriodic acid three, $N_2H_4.HI$, N_2H_42HI, and $3N_2H_4.2HI$.[6] The diacid salts are, however, much less stable than those containing only one equivalent of acid. These salts are described, together with the ammonium salts, in Vol. II. (1897), p. 301.

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[1] de Bruyn, *Rec. Trav. Chim.* 1894, **14**, 82; see also Rothenburg, *Ber.* 1894, **27**, 788.

[2] Curtius and Schulz, *J. pr. Chem.* 1890, [2], **42**, 529.

[3] A. Scott, *Journ. Chem. Soc.* 1904, 913.

[4] Loew, *Ber.* 1890, **23**, 3203.

[5] Tanatar, *Zeit. physikal. Chem.* 1902, **40**, 475; **41**, 37. See also Purgotti and Zanichelli, *Gazzetta*, 1904, **34**, i. 57.

[6] Curtius and Jay, *J. pr. Chem.* 1889, [2], **39**, 33; Curtius and Schultz, *J. pr. Chem.* 1890, [2], **42**, 521.

Hydrazine may be detected by its reducing power and by the characteristic sparingly soluble compounds which it forms with aldehydes, such as benzalazine, $C_6H_5.CH:N.N:CH.C_6H_5$, obtained by shaking an aqueous hydrazine solution with benzaldehyde.

It may be estimated quantitatively by acting on it with Fehling's solution and measuring the nitrogen evolved,[1]

$$4CuO + N_2H_4 = 2Cu_2O + 2H_2O + N_2,$$

or by titrating with iodine in presence of sodium bicarbonate,[2]

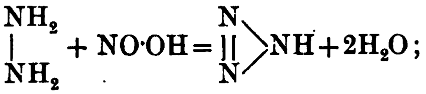
$$N_2H_4 + 2I_2 = N_2 + 4HI.$$

AZOIMIDE OR HYDRAZOIC ACID, N_3H.

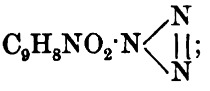
298 This interesting substance was, like the foregoing, discovered by Curtius, who obtained it by the action of nitrites on derivatives of hydrazine, the reaction being analogous to that of nitrites on ammonia. As already mentioned, the interaction of the latter substances leads to the formation of nitrogen, according to the equation

$$NH_4Cl + NaNO_2 = N_2 + 2H_2O + NaCl,$$

and the formation of azoimide is represented in a similar manner by the equation,



$$\begin{matrix}NH_2\\|\\NH_2\end{matrix} + NO{\cdot}OH = \begin{matrix}N\\||\\N\end{matrix}\!\!>NH + 2H_2O;$$

hydrazine itself may be used if only a dilute solution of azoimide is required,[3] but as a rule it is preferable to employ one of its organic derivatives, in which one of the hydrogen atoms is replaced by an organic radical. Curtius in his experiments employed hippurylhydrazine, $C_9H_8NO_2HN{\cdot}NH_2$, which by the action of nitrous acid yields hippurylazoimide,  $C_9H_8NO_2{\cdot}N\!<\!\begin{matrix}N\\||\\N\end{matrix}$; the latter when treated with acids or alkalis is converted into azoimide and hippuric acid.[4] The former distils

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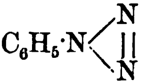
[1] Petersen, *Zeit. anorg. Chem.* 1894, **5**, 1.

[2] Stollé, *J. pr. Chem.* 1902, [2], **66**, 332.

[3] *Ber.* 1893, **26**, 1263.

[4] *Ber.* 1890, **23**, 3023.

over with the water on boiling the solution, which must first be acidified if an alkali has been employed for the hydrolysis.

Numerous derivatives of azoimide in which the hydrogen atom has been replaced by an organic radical had long been known, the most readily prepared of which is the phenyl derivative,  $C_6H_5\cdot N\!<\!\begin{array}{c}N\\ \| \\ N\end{array}$ (Vol. III., Part III., 2nd edition, p. 325), this substance being known as triazobenzene or diazobenzeneimide. This compound itself cannot be converted into azoimide by the action of acids or alkalis, but it has been found[1] that if certain acid radicals such as the group NO_2 be introduced into the phenyl group, the resulting nitro-azoimide may be in many cases converted into the mother substance by the action of alkalis.

Another convenient source of azoimide is the crude amidoguanidine obtained in the preparation of hydrazine (p. 506); this substance is converted by nitrous acid into diazoguanidine nitrate, $NH_2\cdot C(NH)\cdot NH\cdot N{:}N\cdot NO_3$, which on boiling with alkalis yields azoimide and cyanamide; the former may be isolated by acidification and distillation in the manner already described.

A further very interesting synthesis of azoimide from purely inorganic sources has been described by W. Wislicenus,[2] who obtained its sodium salt by the action of nitrous oxide on sodamide:

$$NaNH_2 + N_2O = N_3Na + H_2O.$$

The water formed acts on a further molecule of sodamide yielding caustic soda and ammonia. The sodamide is obtained by passing ammonia over metallic sodium at a temperature of 150—250°, and as soon as all metallic sodium has disappeared, the stream of ammonia is replaced by one of nitrous oxide and continued till ammonia is no longer evolved; the product is then dissolved in water and distilled with dilute sulphuric acid.

Several other interesting modes of formation have also been discovered. A yield of 36 per cent. of the theoretical amount is obtained when a benzene solution of nitrogen chloride (p. 517) is shaken with a solution of hydrazine sulphate, and caustic soda

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[1] Noelting, Grandmougin, and Michel, *Ber.* 1891, **24**, 2546; 1892, **25**, 3328; Tilden and Millar, *Journ. Chem. Soc.* 1893, 256.

[2] *Ber.* 1892, **25**, 2084; See also Szarvasy, *Journ. Chem. Soc.* 1900, 606.

added at intervals.[1] It is also formed when a mixture of molecular proportions of hydrazine and hydroxylamine dissolved in dilute sulphuric acid is oxidised by chromic acid or hydrogen dioxide.[2] The silver salt may also be conveniently prepared by cautiously warming hydrazine sulphate with nitric acid and passing the gas evolved into silver nitrate solution.[3]

The dilute solution obtained by any of the above processes may be concentrated by fractional distillation until the solution contains 91 per cent. of azoimide, and the remainder of the water is then removed by calcium chloride. Pure azoimide forms a colourless mobile liquid which has a most penetrating, unbearable odour, boils without decomposition at 37°, and dissolves readily in water and alcohol. When brought in contact with a hot body it explodes with extreme violence, giving a bright blue flash; the explosion also sometimes takes place at the ordinary temperature, rendering the substance an extremely dangerous one to work with. Thus on one occasion 0·05 gram was introduced into a barometric vacuum, and exploded with such violence that the glass and mercury were reduced to dust and spread over the whole of a large room, and in another case 0·7 gram exploded when taken out of a freezing mixture, breaking all the bottles in the neighbourhood, and somewhat severely injuring one of the investigators.[4]

The acid is slowly decomposed when it is boiled with dilute hydrochloric acid, but is stable in aqueous solution at the ordinary temperature.[5] It is partially reduced by zinc, arsenic, and antimony,[6] and by sodium amalgam, with formation of ammonia and small amounts of hydrazine,[7] whilst potassium permanganate oxidises it completely to water and nitrogen, a variable amount of oxygen being simultaneously evolved.[8] On electrolysis it yields a mixture of 3 volumes of nitrogen with one of hydrogen.[9]

The aqueous solution of azoimide behaves as a strong acid and readily dissolves zinc, iron, magnesium, and aluminium

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[1] Tanatar, *Ber.* 1899, **32**, 1399.

[2] *Ber.* 1902, **35**, 1810.

[3] Sabanieff. *Zeit. anorg. Chem.* 1899, **20**, 21.

[4] Curtius and Radenhausen, *J. pr. Chem.* 1891, [2], **43**, 207.

[5] Curtius and Rissom, *J. pr. Chem.* 1898, [2], **58**, 261.

[6] Curtius and Darapsky, *J. pr. Chem.* 1900, [2], **61**, 408.

[7] Cooke, *Proc. Chem. Soc.* 1903, 213.

[8] Dennis and Browne, *J. Amer. Chem. Soc.* 1904, **26**, 577.

[9] Szarvasy, *Journ. Chem. Soc.* 1900, 603; see also Peratoner and Oddo, *Gazzetta*, 1895, **25**, ii 13.

with evolution of hydrogen and formation of salts of the metals. It also gives salts with the metals of the alkalis and alkaline earths and, like the halogen acids, forms an insoluble *silver* salt, AgN_3, and *mercurous* salt, HgN_3, both of which are extremely explosive, but in other respects closely resemble the corresponding chlorides. The aqueous solution of the acid, as will be seen from the properties already given, behaves chemically in a similar manner to aqueous hydrochloric acid, but in its acid properties and the extent of electrolytic dissociation it corresponds rather with acetic acid.[1] Hence the group N_3 must be itself electronegative, and is analogous in its chemical properties with the halogens.

The salts formed by azoimide with the metals of the alkalis and of the alkaline earths are not nearly so explosive as those formed with the heavy metals, and azoimide itself when in dilute aqueous solution may with reasonable care be handled without danger. The alkali salts give a blood-red coloration with ferric salts, closely resembling that produced by thiocyanates.

Other compounds of nitrogen and hydrogen have been prepared by Curtius; these consist of the salts formed by ammonia and hydrazine with azoimide, and are described with the other ammonium and hydrazine salts (Vol. II. (1897), p. 301).

HYDROXYLAMINE, NH_3O.

299 This compound was discovered in 1865 by Lossen,[2] but until 1891 was only known in the form of salts or in aqueous solution. Lossen obtained it by the action of nascent hydrogen on nitric oxide, the reaction taking place as follows:

$$2NO + 6H = 2NH_3O.$$

Since that time it has been obtained in many other ways, such for example as the reduction of nitric acid by metals under suitable conditions,[3] as a product of decomposition of the fulminates[4] (Vol. III., part I., p. 524), by the action of sulphuretted hydrogen on silver nitrite,[5] by the direct union of

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[1] West, *Journ. Chem. Soc.* 1900, 705.

[2] *Annalen Suppl.* 1868, **6**, 220.

[3] *Journ. Chem. Soc.* 1883, 443.

[4] *J. pr. Chem.* 1882, [2], **25**, 233; *Ber.* 1886, **19**, 993.

[5] *Journ. Chem. Soc.* 1887, 48.

hydrogen with nitric oxide at 115° in presence of platinum black,[1] and by the reduction of sodium nitrite by sodium amalgam.[2]

By the interaction of nitrites and sulphites under suitable conditions, salts of hydroxylaminedisulphonic acid (p. 568) are formed, and these on heating with water are converted into hydroxylamine sulphate (Raschig).[3]

In order to prepare it most economically by means of this reaction[4] a concentrated solution of commercial 95 per cent. sodium nitrite (2 mols.) and sodium carbonate (1 mol.) is treated with sulphur dioxide at −2 to −3° until it is just acid, the liquid being well agitated throughout the operation. The solution, which now contains sodium hydroxylaminedisulphonate, $OH{\cdot}N(SO_3Na)_2$, is warmed with a few drops of sulphuric acid, whereby the salt is hydrolysed to the hydroxylaminemonosulphonate and sodium hydrogen sulphate. The liquid is then kept at 90—95° for two days, during which a further hydrolysis occurs and hydroxylamine sulphate is formed. The solution is neutralised with sodium carbonate, evaporated to a small bulk, and cooled to 0°; sodium sulphate crystallises out, and the mother liquor on evaporation yields hydroxylamine sulphate, which must be once recrystallised and is about equal in weight to the sodium nitrite taken.

Hydroxylamine is now also prepared by the electrolytical reduction of nitric acid, 50 per cent. sulphuric acid being electrolysed with a cathode of amalgamated lead in a cell divided into two compartments, and 50 per cent. nitric acid being gradually run into the cathode compartment.[5]

For a long time free hydroxylamine was known only in solution, but in 1891 the anhydrous compound was prepared almost simultaneously by Lobry de Bruyn[6] and Crismer.[7] The former prepared it by dissolving hydroxylamine hydrochloride in absolute methyl alcohol, adding a solution of sodium methylate, $NaOCH_3$, in the same solvent, separating the sodium chloride formed, and distilling off the greater portion of the methyl alcohol under 100 mm. pressure; the residue is then distilled

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[1] Jouve, *Compt. Rend.* 1899, **128**, 435.

[2] Divers and Haga, *Journ. Chem. Soc.* 1896, 1612.

[3] *Annalen*, 1887, **241**, 161.

[4] Divers and Haga, *Journ. Chem. Soc.* 1896, 1665.

[5] Tafel, *Zeit. anorg. Chem.* 1902, **31**, 289; German Patent 133457.

[6] *Rec. Trav. Chim.* 1890, **10**, 100; **11**, 18.

[7] *Bull. Soc. Chem.* 1891, [3], **6**, 793.

in small portions under 20 mm. pressure with the addition of a little vaseline to prevent frothing. As soon as solid hydroxylamine passes over, the receiver is changed and cooled to 0°, care being taken that the hydroxylamine vapour is not exposed to air at 60—70° for any length of time, as violent explosions then take place. Crismer prepared the base by heating a double compound which it forms with zinc chloride, $ZnCl_2,2NH_2OH$, and it has also been obtained by the distillation of the phosphate at a low pressure.[1]

Hydroxylamine forms white inodorous scales or hard needles, has a sp. gr. of about 1·3, melts at 33·05°, and boils at 58° under 22 mm. pressure, the density of its vapour agreeing with the formula NH_3O. When heated to 90—100° it decomposes, and detonates at a higher temperature. It dissolves readily in water and to a less extent in ethyl and methyl alcohol and in boiling ether, and separates from the last-named solution in acicular crystals on cooling.

It inflames in a current of chlorine gas and combines violently with bromine and iodine, but without evolution of light. In the pure state it is stable below 15°,[2] but in presence of alkali it gradually decomposes, the alkali dissolved from the less resistant forms of glass being sufficient to bring about this change. Strong oxidising agents such as potassium permanganate or bichromate decompose it with production of flame or explosion, and sodium likewise attacks it with production of flame. On exposure to the air it liquefies owing to the absorption of moisture, and then undergoes oxidation with formation of a solid substance containing nitrous acid and ammonia. The solutions have a strongly alkaline reaction, and cause the separation of the more easily reduced metals from their salts. From a solution of copper sulphate it precipitates red cuprous oxide, this reaction being sufficiently delicate to recognise one part of hydroxylamine in 100,000 parts of water.

In the absence of other reducing substances it is best estimated by this reaction, the solution of the base or its salts being added to boiling Fehling's solution;[3] under these circumstances the following reaction occurs:—

$$2NH_3O + 4CuO = N_2O + 3H_2O + 2Cu_2O.$$

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[1] Uhlenhuth, *Annalen*, 1900, **311**, 117.

[2] *Ber.* 1894, **27**, 267.

[3] Jones and Carpenter, *Journ. Chem. Soc.* 1903, 1394.

It can also be titrated in alkaline solution with mercury acetamide, which is reduced by it with formation of metallic mercury.[1]

If sodium nitroprusside be added to a neutralised solution of hydroxylamine, and then a little caustic soda, the whole assumes on boiling a beautiful magenta red colour.[2] When hydroxylamine or its salts are treated with nitrous acid, decomposition takes place rapidly, nitrous oxide being evolved. The reaction proceeds in two stages, hyponitrous acid being first formed according to the equation:

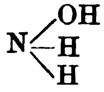
$$HO.NH_2 + ON.OH = HO.N{:}N.OH + H_2O.$$

This substance then rapidly splits up into its anhydride, nitrous oxide, and water (p. 547).[3]

Hydroxylamine can also act as an oxidising agent, being itself reduced to ammonia.[4] Thus in alkaline solution it converts ferrous hydrate into ferric hydrate, whilst in acid solution it reduces ferric chloride to the ferrous salt.[5]

Hydroxylamine is a monacid base forming crystalline salts, such as the hydrochloride $NH_3O.HCl$. These are described after the ammonium salts in Vol. II. (1897), p. 300. They all decompose with effervescence on heating, the nitrate yielding nitric oxide and water:

$$NH_3O,HNO_3 = 2NO + 2H_2O.$$

The behaviour of hydroxylamine towards organic substances shows that it must contain the hydroxyl group OH, and it is therefore ammonia in which one atom of hydrogen is replaced by that group, its constitutional formula being  $N\begin{cases}OH\\H\\H\end{cases}$. This formula is, moreover, in agreement not only with the chemical, but also with the physical properties of the base.[6]

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[1] Forster, *Journ. Chem. Soc.* 1898, 785.

[2] Angeli, *Gazzetta*, 1893, **23**, ii. 102.

[3] Wislicenus, *Ber.* 1893, **26**, 771; Thum *Monatsh.* 1893, **14**, 294.

[4] Biltz, *Ber.* 1896, **29**, 2080.

[5] Haber, *Ber.* 1896, **29**, 2444; Dunstan and Dymond, *Journ. Chem. Soc.* 1887, 646.

[6] Brühl, *Ber.* 1899, **32**, 507; see also Tanatar, *Ber.* 1899, **32**, 241, 1016.

NITROGEN AND THE HALOGENS.

Nitrogen Chloride, NCl_3.

300 This dangerous substance was discovered by Dulong[1] in 1811, who, notwithstanding the fact that he lost one eye and three fingers in the preparation of this body, yet continued its investigation. A similar accident happened in 1813 to Faraday and Davy, who had, however, been made aware of the explosive properties of this substance. "Knowing that the liquid would go off on the slightest provocation, the experimenters wore masks of glass, but this did not save them from injury. In one case Faraday was holding a small tube containing a few grains of it between his finger and thumb, and brought a piece of warm cement near it, when he was suddenly stunned, and on returning to consciousness found himself standing with his hand in the same position but torn by the shattered tube, and the glass of his mask even cut by the projected fragments. Nor was it easy to say when the compound could be relied on, for it seemed very capricious; for instance, one day it rose quickly in vapour in a tube exhausted by the air-pump, but on the next day, when subjected to the same treatment, it exploded with a fearful noise and injuring Sir H. Davy."[2]

The compound is formed by passing chlorine into a warm solution of sal-ammoniac, or when a solution of hypochlorous acid is brought into contact with ammonia (Balard), or by the action of a hypochlorite on sal-ammoniac in presence of some substance, such as benzene, which can dissolve the chloride (Hentschel). If an electric current be passed through a concentrated solution of sal-ammoniac, chloride of nitrogen is formed at the positive pole (Böttger, Kolbe). The liquid obtained by the action of chlorine on a solution of ammonium chloride has been carefully examined by Gattermann, who finds that it is not a single compound, but is a mixture of more or less completely chlorinated ammonias. If, however, it be mixed with a little water and chlorine passed over it for half an hour, it is converted into the completely chlorinated compound NCl_3.[3] The analysis of the liquid was carried out by placing a weighed quantity in water, and carefully adding

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[1] *Schweigg Journ.* 1811, **8**, 302.

[2] Gladstone, *Life of Faraday*, p. 10.

[3] *Ber.* 1888, **21**, 751.

ammonia solution which slowly converts it into nitrogen and ammonium chloride, the chlorine in the solution being then estimated as silver chloride.

Nitrogen chloride is soluble in benzene, chloroform, carbon bisulphide, ether, and other solvents, forming yellow solutions which are stable in the dark but decompose in the light, nitrogen or ammonia and free chlorine, or chlorination products derived from the solvents, being formed.

A 10 per cent. solution in benzene can readily be prepared, and this has been employed for the study of the action of the chloride on organic substances. For this purpose 3 litres of bleaching powder solution, containing 22·5 grams of active chlorine, are treated with hydrochloric acid until the liquid no longer evolves gas when ammonium chloride is added to a sample of it: 300 c.c. of a 20 per cent. solution of ammonium chloride are added and the liquid agitated with 300 c.c. of benzene. The benzene solution is then separated and dried by being poured through a filter containing 20 grams of calcium chloride.[1] This solution can be analysed by exposing it to light and measuring the free nitrogen which is liberated, or by estimating its oxidising effect on arsenious oxide,[2] and it has been found that so long as the ammonium chloride is in excess the substance produced by this method always has the composition NCl_3.

Nitrogen chloride is a thin yellowish oil, which evaporates quickly on exposure to the air, has a sp. gr. of about 1·6, and possesses a peculiar smell, the vapour attacking the eyes and mucous membrane violently. Gattermann has shown that it does not readily explode spontaneously, and may even be subjected to operations such as washing without much risk of explosion, provided direct sunlight is excluded, which at once produces explosion.

When heated by itself to 95°, or if it is brought in contact with certain bodies, such as phosphorus, iodine, or turpentine, it explodes with great violence, giving out light, and pulverising any glass or porcelain vessels in which it may be contained. In cold water it undergoes spontaneous decomposition with the evolution of chlorine, nitrogen, hydrochloric acid, and nitrous acid, hypochlorous acid being also among the primary products of the change.

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[1] Hentschel, *Ber.* 1897, **30**, 1434, 1792, 2642.

[2] Noyes and Lyon, *J. Amer. Chem. Soc.* 1901, **23**, 460.

Nitrogen chloride acts as a chlorinating agent on many organic substances.

The following method is employed for preparing this dangerous substance in small quantities, and for showing its explosive properties without risk. A flask of about two litres capacity, having a long neck, is filled with chlorine, and placed mouth downwards in a large glass basin filled with warm saturated solution of sal-ammoniac as shown in Fig. 133. Below the neck of the flask is placed a small thick leaden saucer, in which the nitrogen chloride is collected. The solution of sal-ammoniac absorbs the chlorine, and, as soon as the flask is three parts filled by the liquid, oily drops are seen to collect on the surface inside the flask. These gradually increase, and at last drop one by one down into the leaden saucer. When a few drops have collected, the leaden saucer may be carefully removed by a pair of clean tongs, another being placed in its stead. A small quantity of the chloride of nitrogen may be exploded by touching it with a feather moistened with turpentine attached to the end of a long rod. Another drop of the oil may be absorbed by filtering paper, and when this is held in a flame a loud explosion likewise ensues.

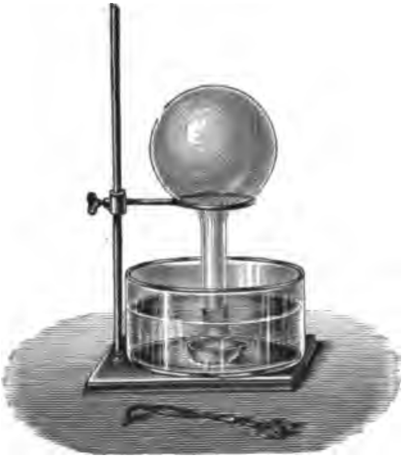

FIG. 133.

The force of the explosion may be rendered still more evident by placing the flask in a strongly constructed box with glass sides, and when the drops of nitrogen chloride collect on the surface of the solution, passing in some turpentine from a stoppered funnel; the latter is kept outside the box and is connected with it by means of rubber and glass tube the end of which dips under the neck of the flask. When the turpentine reaches the surface of the solution in the flask a bright flash is seen, and a violent thunderlike explosion occurs, completely shattering the flask.[1]

The formation and properties of nitrogen chloride may be also exhibited in the following way. A solution of sal-ammoniac, saturated at a temperature of 28°, is brought into a glass basin (A, Fig. 134), and a cylinder (B), the lower end of which is closed by a piece of bladder, is also filled with the solution and placed upright in the basin. A layer of oil of turpentine is then poured on to the top of the liquid in the cylinder, and a platinum plate (*a*) in contact with the positive pole of a battery of six cells is placed in the cylinder, whilst the negative pole (*b*) is placed under the bladder in the basin. Yellow oily drops soon begin to form on the surface of the positive pole, and these gradually become detached from the pole, and rise in the liquid until they come in contact with the layer of turpentine, when they explode.

FIG. 134

Nitrogen Bromide.—When potassium bromide is added to nitrogen chloride under water, potassium chloride and nitrogen bromide are formed. The latter is a dark red very volatile oil, possessing a powerful smell, and is as explosive as nitrogen chloride (Millon).

301 *Nitrogen Iodide.*—When iodine is brought into contact with aqueous or alcoholic ammonia, a black powder is formed which, when dried, decomposes spontaneously with a very violent detonation either when touched or when slightly heated, violet vapours of iodine being emitted (Courtois, 1813). This compound gradually decomposes under cold water, pure

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[1] V. Meyer, *Ber.* 1888, **21**, 26.

iodine being left behind. Warm water facilitates this decomposition, and the body explodes violently when thrown into boiling water.

Much doubt has existed as to the composition of this substance, but Chattaway and Orton have recently shown[1] that only one substance is formed by the action of ammonia on iodine and that its formula is $N_2H_3I_3$, which had previously been obtained in some instances (Bunsen). The varying results of former investigators, which led to formulæ such as NHI_2 (Gladstone, Szuhay, Seliwanow), $NH_3.4NI_3$ (Bunsen), NI_3 (Stahlschmidt), or $N_2H_3I_2$ (Chattaway), are probably to be accounted for by the ease with which the substance decomposes under the influence of light and by the action of water, as well as by the circumstance that all analyses of the substance had been indirect, were carried out with an unknown amount of substance, and yielded only the ratio of the constituents.

It seems probable that in every case nitrogen iodide is formed from ammonium hypoiodite, as was originally suggested by Schönbein and confirmed by Seliwanow,[2] and that this undergoes a spontaneous change represented by the equation:

$$3NH_4OI = N_2H_3I_3 + NH_4{\cdot}OH + 2H_2O.$$

Nitrogen iodide is best prepared pure by the action of ammonia on iodine chloride containing some free hydrochloric acid, a cooled solution of the latter being run slowly into a well stirred mixture of strong ammonia with three times the weight of ice, about 100 c.c. of ammonia being taken for every 10 grams of iodine in the chloride. The black precipitate is then filtered through asbestos and washed with dilute ammonia and finally with a little water, the whole preparation being carried out in a dimly lighted room. A kilogram of the iodide has in this way been obtained in the form of a compact cake with perfect safety, but it should not be allowed to dry and is more stable when the final washing with water is omitted. In this process the ammonia reacts with the iodine chloride to form a mixture of ammonium chloride with hypoiodite,

$$ICl + 2NH_4OH = NH_4Cl + NH_4OI + H_2O,$$

and the latter then undergoes the change which has already

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[1] *Amer. Chem. J.* 1900, **23**, 363; **24**, 342, where a complete list of previous researches on the subject will be found; Chattaway, *Amer. Chem. J.* 1900, **24**, 138.

[2] *Ber.* 1894, **27**, 1012.

been described. The iodide can be obtained in the crystalline form by adding caustic potash to iodine chloride and then adding ammonia. The compound separates slowly in copper coloured crystals; and these can also be obtained by the direct addition of iodine chloride to ammonia, and by warming some of the iodide with ammonia, filtering and cooling. The crystals have the specific gravity 3·5 and when dry are ruby red in colour; they form small flattened needles, probably belonging to the orthorhombic system.

Pure nitrogen iodide can be dried in the dark over baryta in an atmosphere of ammonia, and when dry can be safely detached from a porous tile with a spatula, but is exploded by slight percussion or rapid heating. Partially decomposed iodide is very unstable and explodes at the slightest touch. The pure compound is neutral to litmus paper and imparts no colour to chloroform.

Nitrogen iodide appears also to be formed by the action of liquid ammonia on iodine.[1]

The various reactions and decompositions of nitrogen iodide are readily understood when it is borne in mind that the substance tends to undergo direct decomposition into free nitrogen and hydrogen iodide, and also to be converted by hydrolysis, in the presence of water or acids, into the primary products, ammonia and hypoiodous acid;

$$N_2H_3I_3 = N_2 + 3HI$$
$$N_2H_3I_3 + 3H_2O = 2NH_3 + 3HOI.$$

In nearly all cases both changes proceed simultaneously and secondary reactions then occur. Thus when the compound is washed or heated with water the following change always proceeds in addition to the two primary reactions:

$$HI + HOI = H_2O + I_2.$$

and a certain amount of ammonium iodate is sometimes formed.[2]

Light readily brings about the decomposition of the substance into nitrogen and hydriodic acid, free iodine being also produced by the action of the hydriodic acid on the unaltered substance. The explosive decomposition of the iodide is probably also due to this same change.[3]

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[1] Hugot, *Compt. Rend.* 1900, **130**, 505; Ruff, *Ber.* 1900, **33**, 3025.

[2] Chattaway and Orton, *Amer. Chem. J.* 1900, **24**, 318. Chattaway and Stevens, *Amer. Chem. J.* 1900, **24**, 331.

[3] Chattaway and Orton, *Amer. Chem. J.* 1900, **24**, 159.

Nitrogen iodide is an active oxidising agent, converting sulphites into sulphates, arsenious acid into arsenic acid, and sulphuretted hydrogen into sulphur and water.[1] In each case the oxidising effect of one atom of oxygen is exerted by each atom of iodine in the iodide, exactly as would be the case were hypoiodous acid the direct oxidising agent. The reaction with sodium sulphite,

$$N_2H_3I_3 + 3Na_2SO_3 + 3H_2O = 3Na_2SO_4 + 2NH_4I + HI,$$

has been employed for the analysis of the pure compound. For this purpose a weighed amount of the latter is titrated with the sodium sulphite until all iodine has disappeared, and the amount of free acid produced and the total amount of iodine present are then estimated by titration with baryta and silver nitrate respectively. In this way it has been shown that the substance formed by the action of ammonia on iodine is in all cases the same, $N_2H_3I_3$, when care is taken to avoid all decomposition.

Iodoazoimide, N_3I, is formed by the action of an ethereal solution of iodine on silver azoimide at 0°. It is a nearly colourless solid which readily explodes, forming free nitrogen and iodine.[2]

NITROGEN AND OXYGEN.

OXIDES AND OXY-ACIDS OF NITROGEN.

302 As already mentioned, nitrogen burns in oxygen when both gases are heated to a sufficiently high temperature (p. 490), and direct combination also takes place more slowly when a series of electric sparks is passed through fairly dry air, whilst if much moisture is present nitric acid is produced. When a mixture of nitrogen and oxygen is passed over platinum black at 250°, oxides of nitrogen are also formed,[3] and they are further produced when carbon is burnt in highly compressed air[4] and in small quantities during almost all processes of combustion in air.[5] We are acquainted with five oxides of nitrogen,[6] and four

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[1] Chattaway and Stevens, *Amer. Chem. J.* 1900, **23**, 369.

[2] Hantzsch, *Ber.* 1900, **33**, 522.

[3] Loew, *Ber.* 1890, **23**, 1443.

[4] Hempel, *Ber.* 1890, **23**, 1457.

[5] Berthelot, *Compt. Rend.* 1900, **130**, 1345, 1430, 1662.

[6] According to Berthelot and Hautefeuille and Chappuis, a sixth oxide, possessing the composition N_2O_6, exists. It is formed by the action of an electric

oxygen acids corresponding to the oxides numbered 1, 2, 3, and 5.

Oxides.		Acids.	
1. Nitrous Oxide, or Nitrogen Monoxide	$\left.\begin{matrix}N\\N\end{matrix}\right\}O$	Hyponitrous Acid.	$\left.\begin{matrix}HO.N\\HO.N\end{matrix}\right\}$
2. Nitric Oxide, or Nitrogen Dioxide	NO	Nitrohydroxylamic Acid . .	$HON{:}NO_2H$.
3. Nitrogen Trioxide	$\left.\begin{matrix}NO\\NO\end{matrix}\right\}O$	Nitrous Acid . .	$\left.\begin{matrix}NO\\H\end{matrix}\right\}O$
4. Nitrogen Peroxide, or Nitrogen Tetroxide	NO_2		
5. Nitrogen Pentoxide	$\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$	Nitric Acid . . .	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$

NITRIC ACID, HNO_3.

303 In the Latin Geber's tract, *De Inventione Veritatis*, we find the following description of a mode of preparing nitric acid or aquafortis:—"Sume libram unam de vitrioli de cypro, et libram salis petræ, et unam quartam aluminis Jameni, extrahe aquam (the acid) cum rubidine alembici." That is, by strongly heating a mixture of saltpetre, alum, and sulphate of copper, the nitric acid distils over, owing to the decomposition of the saltpetre by the sulphuric acid of the other salts. Nitric acid was commonly prepared and used as a valuable reagent by the alchemists, especially as a means of separating gold and silver. The method of preparation which we now use from nitre and oil of vitriol appears to have been first employed by Glauber, for long afterwards the acid thus obtained was called *spiritus nitri fumans Glauberi*.

The first theory respecting the composition of nitric acid was proposed by Mayow in 1669.[1] He believed that the acid contained two components, one derived from the air and having a fiery nature and the other derived from the earth. More than a century later, in 1776, Lavoisier showed that one constituent of nitric acid is oxygen, but he was unable to satisfy himself as to the nature of the other components, and it was reserved for Cavendish[2] to prove the exact composition and mode of formation of this acid or its salts by the direct

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discharge on a mixture of nitrogen peroxide and oxygen. (See *Ann. Chim. Phys.* [5], 1881, **22**, 432; *Compt. Rend.* 1881, **92**, 80, 134; 1882, **94**, 1111, 1306.)

[1] Mayow, *De sal-nitro et spiritu nitro-aereo.*

[2] *Phil. Trans.* 1784, 119; 1785, 372.

combination of oxygen and nitrogen gases in presence of water or alkaline solutions. Priestley had already observed that when a series of electric sparks was made to pass through common air included between short columns of a solution of litmus, the solution acquired a red colour and the air was diminished in volume. Cavendish repeated the experiment, using lime-water and soap-lees (caustic potash) in place of the litmus, and he concluded that the lime-water and soap-lees became saturated with some acid formed during the operation. He proved that this was nitric acid by passing the electric discharge through a mixture of pure dephlogisticated air (oxygen) and pure phlogisticated air (nitrogen) over soap-lees (caustic potash), when nitre (potassium nitrate) was formed. Cavendish[1] clearly expresses his views in the following words:—"We may safely conclude that in the present experiments the phlogisticated was enabled, by means of the electric spark, to unite to, or form a chemical combination with, the dephlogisticated air, and was thereby reduced to nitrous acid, which united to the soap-lees and formed a solution of nitre; for in these experiments those two airs actually disappeared, and nitrous acid was actually formed in their room." The apparatus which he employed, represented in Fig. 135, consisted of a bent syphon-tube containing, in the bent portion, the mixture of gases and mercury in the limbs, the open ends dipping under mercury in the glasses.

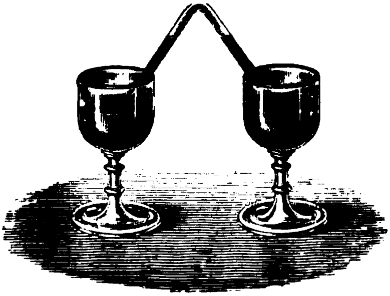

FIG. 135.

Nitric acid is also formed when various bodies are burnt in a mixture of oxygen and nitrogen. Thus, if three to five volumes of the detonating mixture of oxygen and hydrogen be mixed with one volume of air in a eudiometer over mercury, and an electric spark passed through the mixture, instantaneous

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[1] *Phil. Trans.* 1785, 379.

combination takes place and some nitric acid is formed, the surface of the mercury becoming covered with crystals of mercurous nitrate.[1]

In order to exhibit the direct combination of oxygen and nitrogen it is only necessary to allow the sparks from an induction-coil to pass between two platinum wires placed in the interior of a large glass globe containing dry air, as shown in Fig. 136. Red fumes of nitrogen peroxide are rapidly formed, and their presence may be distinctly recognised by plunging a piece of iodised starch-paper into the globe, when the blue iodide of starch will at once be produced. On pouring a few drops of water into the globe and shaking it up, the red fumes are absorbed and nitrous and nitric acids formed, as may be shown by the acid reaction of the liquid.

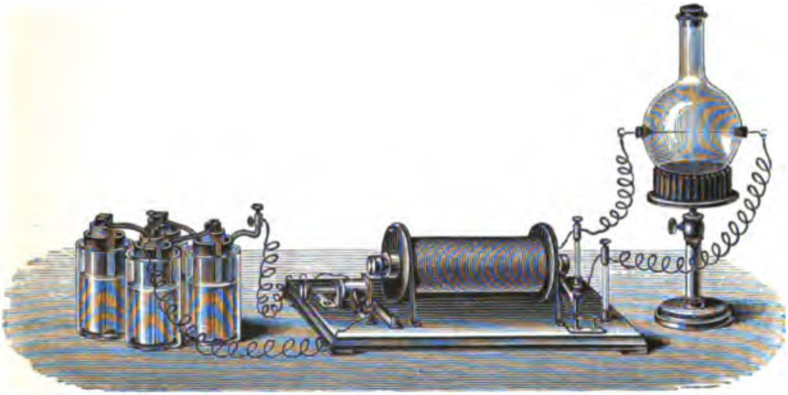

FIG. 136.

In a similar manner, if a flame of hydrogen be allowed to burn in a large flask into which oxygen is led, but not in such quantity as to displace the whole of the air, nitric acid is formed in large quantity.[2] The same acid is also produced when ammonia burns in oxygen. The formation of nitric acid by the discharge of electricity through the air accounts for the presence of this acid in the atmosphere.

Another and more productive source of the nitrates has yet to be described. When nitrogenous organic matter is exposed to the air the nitrogen assumes the form of ammonia; but when alkalis, such as potash, soda, or lime, are present a further slow

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[1] Bunsen, *Gasometry*, p. 58.

[2] Kolbe, *Annalen*, 1861, **119**, 176; Hofmann, *Ber.* 1870, **3**, 663.

oxidation of the nitrogen takes place, and nitrates of these metals are formed, the change in both cases being due to the action of bacteria. Hence these nitrates are widely diffused in all surface soils, especially in hot countries such as India, where oxidation takes place quickly. Soil in the neighbourhood of Indian villages, which contains considerable amounts of potash, thus becomes rich in nitre or potassium nitrate, KNO_3, originating from the decomposition of the urea of the urine. It is from this source that the largest quantity of nitre imported into this country is obtained. Another nitrate, lime-saltpetre or calcium nitrate, $Ca(NO_3)_2$, is often found as an efflorescence on the walls of buildings, such as stables, or cellars of inhabited houses, and this source was made use of during the French Revolution for the manufacture of nitre. Chili saltpetre, or sodium nitrate, $NaNO_3$, occurs in large deposits in the province of Tarapaca, a rainless district on the Peruvian coast lying near the 20th degree of south latitude. The sodium nitrate is found mixed with chloride of sodium and other salts, probably pointing to the fact that the locality has been covered by the sea, and that the nitrate is a product of the decomposition of sea-plants and animals.

304 *Preparation.*—In order to prepare pure nitric acid, saltpetre which has been previously well dried is placed in a tubulated retort together with an equal weight of concentrated sulphuric acid. On heating the mixture, the volatile nitric acid passes over, and is collected in a well-cooled receiver, see Fig. 137, hydrogen potassium sulphate (commonly called bisulphate of potash) remaining behind in the retort; thus:—

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4.$$

The distillate thus obtained has a yellowish colour, caused by the presence of nitrogen peroxide, and it is not free from water, as the concentrated acid, when heated, decomposes partially into peroxide, oxygen, and water. In order to purify the acid thus obtained it must be again distilled with its own volume of concentrated sulphuric acid, and the distillate freed from traces of the peroxide by gently warming the acid, and leading a current of dry air through it until it is cold. Thus prepared it contains from 99·5 to 99·8 per cent. of the anhydrous acid, HNO_3.

To obtain an acid of still greater concentration[1] and containing less impurity the concentrated acid is distilled under dimin-

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[1] Veley and Manley, *Phil. Trans.* 1898, (A) 191, 365.

ished pressure with a small amount of barium nitrate and of silver nitrate to remove traces of sulphuric and hydrochloric acids, and the distillate is then treated with a stream of ozonised oxygen to remove nitrous acid, the liquid being again distilled under diminished pressure. Finally this distillate is redistilled in a sealed and evacuated apparatus, the product being pure anhydrous nitric acid.

305 *Properties.*—Nitric acid is a colourless liquid fuming strongly in the air, which boils at 86°, or 78·2° according to Aston and Ramsay, and solidifies at 47°. It possesses a peculiar though not very powerful smell, and absorbs moisture from the air with the greatest avidity. Nitric acid is an extremely corrosive substance, which, when brought in contact with the skin, produces painful wounds, being used in surgery as a powerful cautery. The dilute acid acts less energetically, and colours the skin, nails, wool, silk, and other organic bodies a bright yellow tint.

FIG. 137.

When pure concentrated nitric acid is heated, it begins to boil at 78·2°, and becomes of a dark yellow colour owing to the decomposition of a portion of the acid into nitrogen peroxide, oxygen, and water. As soon as about three-fourths of the acid has distilled over, the residue becomes colourless, and then contains only 95·8 per cent. of acid.[1] If the distillation is pushed further, the boiling point continually rises, a strong acid distils over, and the residue becomes constantly weaker until it contains 68 per cent. of acid, when the liquid is

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[1] Roscoe, *Journ. Chem. Soc.* 1861, 147.

found to boil unaltered at 120·5° under the normal atmospheric pressure, yielding an acid of the above constant composition and with a specific gravity of 1·414 at 15·5°. This constant acid is always obtained, whether a stronger or a weaker acid be subjected to distillation. If this acid of constant composition be distilled under an increased, or under a diminished pressure, the composition of the residual acid again undergoes a change, until for each pressure a constant boiling point is reached. Thus, under the pressure of 1·22m. of mercury, an acid containing 68·6 per cent. of HNO_3 distils without alteration, whilst under a pressure of 0·070m. an acid distils over at a temperature of from 65 to 70°, having a constant composition of 66·7 per cent. When a current of dry air is passed through aqueous nitric acid, either a stronger or a weaker acid is volatilised, according to the concentration or the temperature of the acid, until at length a residue is obtained which volatilises unchanged. Thus, when the experiment is made at 100°, the residual acid contains 66·2 per cent.; when at 60°, 64·5 per cent.; and at 15° the residual acid contains 64·0 per cent. of HNO_3. From this it will be seen that nitric acid behaves in a similar way in this respect to hydrochloric and the other aqueous acids.

When the concentrated acid is mixed with water an increase of temperature and a contraction of bulk is observed. The following table gives the specific gravities of aqueous acids at 15/4° (Lunge and Rey):[1]—

Sp. gr. at 15/4°.	Per cent. HNO_3.	Sp. gr. at 15/4°.	Per cent. HNO_3.
1·025	4·60	1·325	51·53
1·050	8·99	1·350	55·79
1·075	13·15	1·375	60·30
1·100	17·11	1·400	65·30
1·125	21·00	1·425	70·98
1·150	24·84	1·450	77·28
1·175	28·63	1·475	84·45
1·200	32·36	1·500	94·09
1·225	36·03	1·510	98·10
1·250	39·82	1·515	99·07
1·275	43·64	1·520	99·67
1·300	47·49		

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[1] *Zeit. angew. Chem.* 1891, 167; 1892, 10; see also Veley, *J. Soc. Chem. Ind.* 1903, **22**, 1227, for the densities of concentrated nitric acid.

Hydrates of Nitric Acid.—Pickering has succeeded in isolating two hydrates of nitric acid, having the composition $HNO_3,3H_2O$ and HNO_3,H_2O respectively. The former separates in large, fairly transparent crystals melting at −18·2°, and the latter in smaller, more opaque, gritty crystals[1] melting at −36·8°, or according to Küster and Kremann[2] at −38°. These appear to be the only hydrates of the existence of which there is definite evidence (see p. 532).

Concentrated nitric acid begins to decompose even at temperatures below 78·2°, into water, oxygen, and nitrogen peroxide.

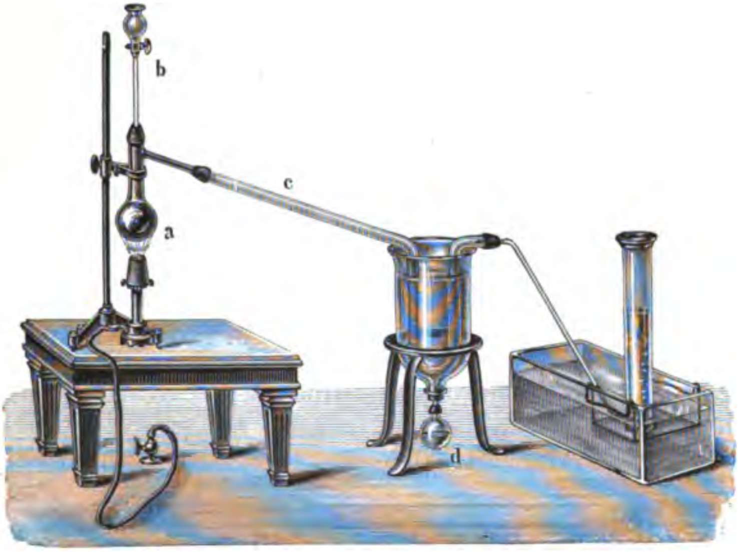

FIG. 138.

If the acid be more strongly heated in closed glass tubes this change takes place so rapidly that at 260° the whole of the nitric acid is thus decomposed (Carius).

In order to exhibit this decomposition by means of heat, the apparatus shown in Fig. 138 is employed. Strong nitric acid is allowed to fall on hot pumice-stone contained in the platinum flask (*a*). Immediately red vapours are emitted, and these are condensed in a U-tube placed in a freezing mixture to a brown liquid, N_2O_4, whilst the cylinder placed over the

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[1] *Journ. Chem. Soc.* 1893, 439.

[2] *Zeit. anorg. Chem.* 1904, **41**, 1.

pneumatic trough becomes filled with a colourless gas which can be easily shown to be oxygen (Hofmann).

A similar decomposition occurs when the concentrated acid is exposed to light.[1]

306 Nitric acid is a monobasic acid forming a series of salts which are termed the *nitrates*. These are almost all easily soluble in water, and as a rule crystallise well. They may be obtained by neutralising the acid with an oxide or a carbonate, and are almost all formed by dissolving the metal in nitric acid. In this case the metal is oxidised at the expense of a portion of the acid, which, according to the concentration or the temperature, is reduced to NO_2, N_2O_3, NO, N_2O, and even to nitrogen and ammonia.

Many other bodies, such as sulphur, phosphorus, carbon, and many organic substances, are easily oxidised, especially by the concentrated acid. In order to exhibit this action, some nitric acid may be poured upon granulated tin, which is then oxidised with the evolution of dense red fumes, whilst a white powder of tin oxide is deposited. Turpentine when poured into the concentrated acid is likewise oxidised with almost explosive violence, light and heat being evolved. In like manner ignition may take place when straw or sawdust becomes impregnated with the strong acid.

Other organic bodies treated with nitric acid undergo no apparent alteration. Thus, for instance, with cotton-wool no ignition or evolution of red fumes occurs. If, however, the cotton-wool after having been thus soaked in strong nitric acid is washed and dried, it is found to possess very different properties from ordinary cotton, although in appearance it can hardly be distinguished from it. Cotton-wool, or cellulose, has the formula $(C_{12}H_{20}O_{10})_n$, whilst after treatment with nitric acid it consists of nitro-cellulose, gun-cotton or collodion-cotton. This consists of cellulose in which some of the hydroxyl groups, varying in number from four to six according to the strength of nitric acid employed, are replaced by NO_3, the changes which have occurred being represented by the equation:—

$$C_{12}H_{20}O_{10} + 4HNO_3 = C_{12}H_{16}O_6(NO_3)_4 + 4H_2O,$$
$$\text{or } C_{12}H_{20}O_{10} + 6HNO_3 = C_{12}H_{14}O_4(NO_3)_6 + 6H_2O.$$

Nitric acid acts in a similar way on many other organic bodies.

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[1] Berthelot, *Compt. Rend.* 1898, **127**, 143.

307 *Action of Nitric Acid on Metals.*—As already mentioned, nitric acid dissolves a large number of metals with formation of nitrates. Hydrogen is not evolved at the same time, as is the case with sulphuric and hydrochloric acids, but in its place lower oxides of nitrogen and even nitrogen itself and ammonia are formed. The explanation frequently given of this change is that hydrogen is first produced, but that it at once acts on the excess of nitric acid present, forming water and the lower oxides of nitrogen. Thus, for example, the formation of nitric oxide by the action of copper on nitric acid is supposed to take place in the two following stages:—

$$Cu + 2HNO_3 = Cu(NO_3)_2 + 2H$$
$$6H + 2HNO_3 = 2NO + 4H_2O.$$

According to Veley, however, this explanation is not correct, inasmuch as pure copper, mercury, and bismuth do not dissolve in pure dilute nitric acid, but dissolve readily when nitrous acid is present, the change at any moment being directly proportional to the mass of nitrous acid in the solution, and the more rapid the greater the proportion of the former to the latter. He therefore believes that the reaction is started either by traces of nitrous acid already present, or by impurities in the metal inducing a local electric current; the first product of the reduction of the nitric acid is nitrous acid, and the production of lower oxides of nitrogen he regards as due to the subsequent changes occurring between nitrous acid and the metallic nitrate or nitrite in presence of an excess of nitric acid, the nitrous acid being decomposed as fast as it is formed.[1]

The relative proportion of the products formed varies not only with the concentration of the acid and the temperature, but also with the nature of the metal employed. Thus silver when treated with acids of sp. gr. 1·05—1·4 yields nitric oxide and nitrogen peroxide, but no nitrous oxide, whereas lead with an acid of sp. gr. 1·2 yields a gas of which 40 per cent. is nitrous oxide.[2]

308 *Constitution of Concentrated Nitric Acid.*—Pure anhydrous nitric acid has no action on the metals copper, silver, cadmium,

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[1] *Proc. Roy. Soc.* 1890, **46**, 216; 1893, **52**, 27; *Phil. Trans.* 1891, (A) 312; *J. Soc. Chem. Ind.* 1891, **10**, 204.

[2] Freer and Higley, *Amer. Chem. J.* 1893, **15**, 71; 1899, **21**, 377; Higley, *Amer. Chem. J.* 1895, **17**, 18; Higley and Davis, *Amer. Chem. J.* 1896, **18**, 587.

and mercury, but causes sodium to take fire. It has no action on calcium carbonate even at the boiling point, but readily oxidises sulphur and sulphides, nitrates benzene, and also converts cellulose into nitrocellulose. This behaviour renders it probable that in the pure state nitric acid exists in the bimolecular form $H_2N_2O_6$, which has no acid properties,[1] and this agrees with the molecular weight of the liquid[2] as determined from the molecular surface energy at different temperatures (p. 113).

The physical properties of concentrated solutions of nitric acid, which have been examined with great care by Veley[3] and others, seem to indicate the presence of various hydrates in the liquid, and two have, as already mentioned, been actually isolated. Some chemists formulate the monohydrate as orthonitric acid, H_3NO_4 or $NO(OH)_3$, and regard the more concentrated acids as mixtures of this with the bimolecular form of nitric acid,[4] but the evidence upon which this view is based cannot at present be regarded as conclusive.

309 *Commercial Manufacture.*—Nitric acid is employed in large quantities in the manufacture of sulphuric acid (p. 414), in the preparation of the coal-tar colouring-matters, and especially in the manufacture of explosives, such as nitroglycerine and gun-cotton, and the combinations of these which form the different varieties of smokeless powder. Smaller quantities are employed in the preparation of silver nitrate for use in photography, and in the manufacture of certain nitrates, such as those of lead, iron, and aluminium, which are employed in the processes of dyeing and calico-printing, whilst the nitrates of strontium and barium are used for pyrotechnic purposes. It is an indispensable reagent in the laboratory, and is used in the preparation of a large number of inorganic and organic substances.

In the manufacture of the acid, the reaction already described for its preparation on the small scale is employed, but the cheaper sodium nitrate or Chili-saltpetre is usually

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[1] Veley and Manley, *Proc. Roy. Soc.* 1897, **62**, 223; *Journ. Chem. Soc.* 1903, 1015.

[2] Aston and Ramsay, *Journ. Chem. Soc.* 1894, 169.

[3] Veley, *Ber.* 1895, **28**, 928; *Proc. Roy. Soc.* 1901, **69**, 86; Veley and Manley, *Proc. Roy. Soc.* 1897, **62**, 223; 1901, **68**, 128; *Phil. Mag.* 1902, [6], **3**, 118; *Journ. Chem. Soc.* 1903, 1015; *Phil. Trans.* 1898, (A) **191**, 365. See also Erdmann, *Zeit. anorg. Chem.* 1902, **32**, 431; *Ber.* 1902, **35**, 2526; Küster, *Chem Zeit.* 1904, **28**, 132; Küster and Kremann, *Zeit. anorg. Chem.* 1904, **41**, 1.

[4] Hartley, *Journ. Chem. Soc.* 1903, 658.

substituted for the more expensive nitre. Sulphuric acid acts on the sodium nitrate in the first instance, forming nitric acid and sodium hydrogen sulphate (frequently termed bisulphate);

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4.$$

At a higher temperature the latter is capable of reacting with a further molecule of nitrate with formation of nitric acid and normal sodium sulphate;

$$NaHSO_4 + NaNO_3 = HNO_3 + Na_2SO_4.$$

In practice, however, only the first reaction is carried out, as, owing to the higher temperature required for the second reaction, the wear and tear of the apparatus is much greater, and the nitric acid formed is decomposed to a greater extent into water, nitrogen peroxide, and oxygen; further, whereas sodium bisulphate is liquid at moderate temperatures, the normal sulphate is solid and is much more difficult to remove after the completion of the reaction, so that the increased cost of working more than counterbalances the saving in sulphuric acid used when the second reaction is carried out. Generally about equal weights of Chili-saltpetre and concentrated sulphuric acid are employed or, if weaker acid be used, a quantity of the latter is taken containing the above amount of pure acid. When acid of the highest strength is required, the nitrate, which usually contains about 3 per cent. of moisture, is dried before use.

The decomposition is carried out in horizontal cylinders or stills set in a suitable furnace and constructed of cast-iron, as this metal, when of proper quality and free from blowholes, is only slightly acted upon, provided that it is maintained sufficiently hot throughout to prevent the condensation of liquid nitric acid on the surface. Fig. 139 shows the construction of a cylinder, the ends of which are luted in, the front one being removable for charging the saltpetre. After this has been done, the sulphuric acid is run in through the socket in the front end, the acid vapours passing away through the corresponding socket in the back; when the reaction is complete, the front cover is removed, and the sodium bisulphate drawn out. Fig. 140 represents a form of still employed for large charges, the nitrate being introduced through the large opening *b*, which is then closed by a luted stopper, in the centre of which is an opening for running in the sulphuric acid, the acid vapours passing away by the pipe *b′*. On the completion of the reaction, which requires about 24 hours with a charge of 12 cwt., the bisulphate is run off whilst still liquid by the discharge pipe E.

The condensation of the acid vapours was formerly carried out by passing them through a series of stoneware Woulfe's bottles, the uncondensed vapours then traversing a coke tower

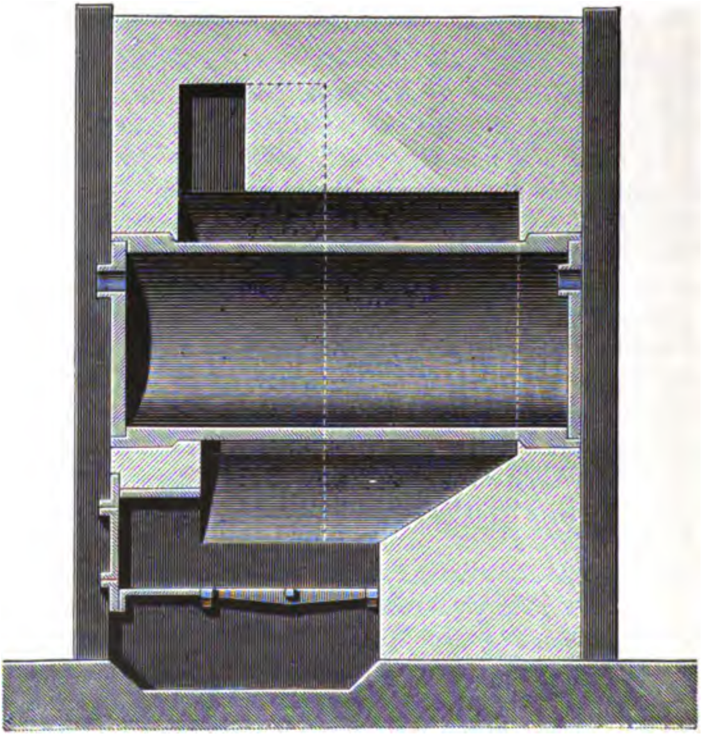

FIG. 139.

down which water trickles; and this method is still largely adopted. The acid thus produced contains many impurities, especially nitrogen peroxide and halogen compounds derived from the iodine and chlorine present in the Chili-saltpetre. Improved methods of cooling are, however, now frequently employed. In the condensation system devised by Guttmann, the Woulfe's bottles are replaced by a series of special earthenware pipes, arranged in a similar manner to the well-known vertical atmospheric condensers used in gasworks, and, in order to reduce the amount of nitrogen peroxide to a minimum, compressed air is admitted into the acid vapours leaving the still, the oxygen of the latter together with the moisture always present converting this largely into nitric acid. Where concentrated acid is required, the temperature of the condenser is so regulated as to bring about the condensation of nitric acid only, which is allowed to flow away at once from the bottom of each pipe so as to avoid contaminating it with the impurities present in the uncondensed vapours. The bulk of the steam, nitrogen peroxide, and other impurities pass through the condenser without liquefying, and then traverse a Lunge-tower (p. 416), in which they meet a stream of water, yielding a dilute

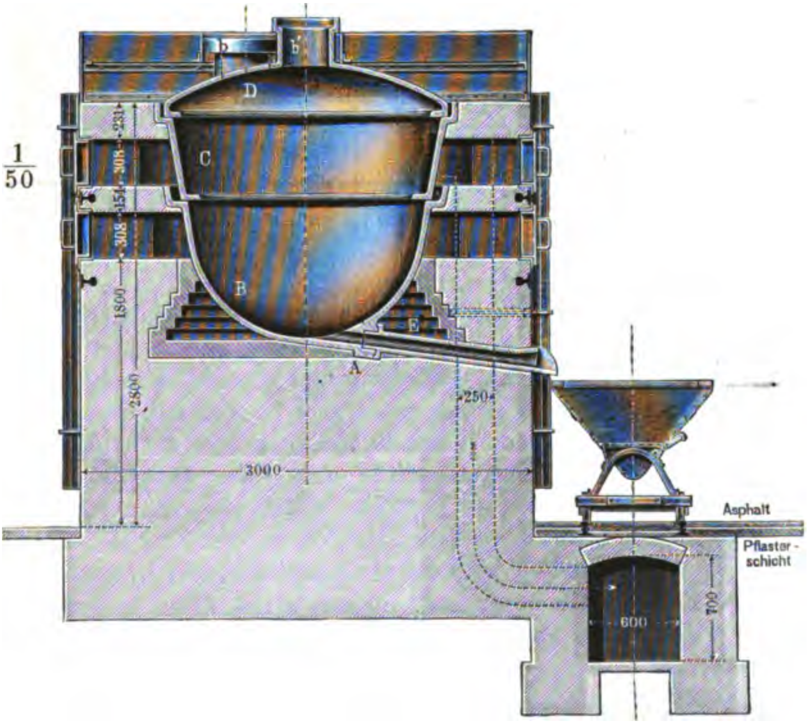

Fig. 140.

impure acid. In this manner, acid of 97 per cent. strength and containing only 0·7 per cent. of nitrogen peroxide is obtained from the condensers.

Where a more dilute acid is required, the Guttmann condensation pipes may be cooled in a tank of water, whereby the rate of condensation is greatly increased; the acid in this case contains a rather higher percentage of nitrogen peroxide.

A continuous process for the production of nitric acid has been devised by Prentice.[1] The apparatus consists of an oblong trough, heated in a furnace, and divided laterally by partitions which are perforated at the bottom to allow of the passage of the liquid from compartment to compartment, the acid vapours evolved being carried off separately from each of the latter into a trunk main. The nitrate and acid, the latter being present in an excess of at least 20 per cent., enter continuously at one end, and flow from compartment to compartment to the other end of the trough, from which the bisulphate flows away freed from nitric acid.

A further modification has been introduced by Valentiner,[2] who carries out the decomposition of the nitrate and condensation of the acid in a partial vacuum, whereby it is claimed that a purer and more concentrated acid is obtained, owing to the lower temperature at which the decomposition takes place.[3]

Ordinary red commercial nitric acid owes its colour to the presence of nitrogen peroxide, which may be removed by passing a current of air through the warmed acid for 48 hours, the vapours carried off with the air being recovered by passing them through a coke or Lunge-tower, where they are washed out with water, the process being termed *bleaching*. The commercial acid also contains chlorine and frequently iodic acid, originating from the Chili-saltpetre, as well as iron, sulphuric acid, and sodium sulphate, which have been mechanically carried over. To free the acid from these impurities it may be distilled in a glass retort, chlorine, nitrosyl chloride, and nitrogen peroxide coming over with the first portion. As soon as the distillate is free from chlorine the receiver is changed, and the liquid may then be distilled until only a small residue remains,

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[1] *J. Chem. Soc. Ind.* 1894, **13**, 323.

[2] Engl. Patent, No. 610 (1892); 19192 (1895).

[3] For further information as to the manufacture, see Guttmann, *Manufacture of Explosives* (Whittaker, 1895), p. 126; Muspratt's *Encykl. d. Tech. Chem.* **7**, 647; Lunge's *Sulphuric Acid* (1903), p. 104.

which contains the whole of the iodic acid, sulphuric acid, and sodium sulphate.

Manufacture of Nitric Acid from Ammonia.—It has long been known that nitric acid and the higher oxides of nitrogen are formed by the oxidation of ammonia with oxygen in presence of various catalytic agents such as platinum, and Ostwald[1] has recently introduced a process in which this reaction is utilised for the commercial production of nitric acid. A mixture of ammonia and air is obtained by treating the latter with gas-liquor or other liquid containing ammonia, the counter-current principle being employed, according to which the fresh air is exposed to the action of nearly spent liquor, whilst the ammonia laden air is finally passed through fresh liquor. The mixture of air and ammonia is then passed through a catalytic furnace containing platinum and maintained at a red heat. Nitric acid or higher oxides of nitrogen are thus produced, and are recovered by means similar to those already mentioned. To obtain good results, compact platinum is employed, a portion of the surface of which is covered with platinum sponge or black; the presence of the latter accelerates the reaction, but if the whole of the platinum be in this form, the ammonia is to a considerable extent converted into free nitrogen instead of the oxides.

Manufacture of Nitric Acid from Atmospheric Air.—It has already been stated (p. 490) that nitrogen and oxygen combine together when an electric discharge is passed through the mixed gases, and many attempts have been made to utilise this method for the manufacture of nitric acid from atmospheric air. At the present time the process is being carried out at the Niagara Falls, according to a method patented by Bradley and Lovejoy,[2] in which air, previously cooled and dried, is subjected to the action of a series of rapidly interrupted arcs. The electromotive force employed is 10,000 volts, and the arcs are formed and broken at the rate of 414,000 per minute. Under these circumstances it is stated that the resulting gaseous mixture contains 2·5 per cent. of oxides of nitrogen, which are recovered as nitric acid by passing them through a condensing tower down which water flows. It is claimed that the acid obtained is perfectly pure, and that it is produced at less cost by this means than by any other process.

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[1] Engl. Patent, No. 698 (1902).

[2] U.S. Patent, 709, 867 (1902); *Electrician*, 1902, 684.

310 *Detection and Estimation.*—The presence of nitric acid or of its salts is easily ascertained. Thus, for instance, if we heat a few drops of not too dilute nitric acid with copper turnings, brownish-red vapours of nitrogen peroxide are emitted. The nitrates give the same reaction if they, or their concentrated aqueous solutions, are treated with sulphuric acid and copper. In order to detect nitric acid or a nitrate in a very dilute solution, a cold solution of ferrous sulphate is added to the liquid, and about an equal volume of strong sulphuric acid is then allowed to flow slowly down to the bottom of the inclined test-tube, care being taken that the two liquids do not mix. If nitric acid be present it is liberated by the action of the sulphuric acid, and at once oxidises the ferrous sulphate where it comes in contact with it, nitric oxide being simultaneously given off. The latter at once unites with the excess of ferrous sulphate forming a dark brown compound, the solution of which is seen as a dark-coloured ring at the point where the dense sulphuric acid joins the lighter aqueous solution.

The organic base called brucine, bearing a close resemblance to strychnine, also serves as a test for nitric acid. If to half a drop of a solution of one part of nitric acid in 100,000 parts of water, one or two drops of a solution of brucine be added, and then a few drops of concentrated sulphuric acid, a distinct pink coloration will be observed if the solution be viewed against a white ground.[1]

If nitrites are present they must be removed before the foregoing tests are applied, and this is best effected by evaporating the neutral solution with ammonium chloride.

In order quantitatively to determine the amount of nitric acid contained in potassium- or sodium-saltpetre, the well-dried substance is heated to dull redness for half an hour with freshly-ignited and finely-powdered quartz or silica, SiO_2. The nitrates are thus completely decomposed, whilst any sulphates or chlorides which may be present undergo no change. The decomposition which here takes place may be represented as follows:—

$$2KNO_3 = K_2O + 2NO_2 + O.$$

Oxygen and nitrogen peroxide are evolved, whilst the potash combines with the silica to form potassium silicate. From the loss of weight thus ensuing the amount of nitre present can easily be calculated.

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[1] Reichardt, *Jahresbericht*, 1871, 893.

Another good method, which is particularly useful in the determination of the nitrates contained in drinking-water, depends upon the fact that a thin zinc plate, which has been covered with a deposit of spongy metallic copper by dipping it into a solution of copper sulphate, on being heated with water containing nitrates reduces them to ammonia, zinc hydroxide and free hydrogen being at the same time formed (Gladstone and Tribe); thus:—

$$KNO_3+8H=NH_3+KOH+2H_2O.$$

The reduction may also be effected by aluminium and caustic soda. The ammonia thus obtained is distilled over into an excess of hydrochloric acid and determined in the usual way, or if present in only small quantities by nesslerisation (see p. 324).

Another method, proposed by Lunge, consists in mixing the nitrate with sulphuric acid and shaking in a graduated tube with mercury; the whole of the nitrogen is liberated in the form of nitric oxide, the volume of which is measured. The reaction which takes place is represented by the following equation:—

$$3Hg+3H_2SO_4+2HNO_3=3HgSO_4+4H_2O+2NO.$$

A special apparatus known as the nitrometer has been designed by Lunge for carrying out this reaction[1] which is especially useful in the determination of the nitrogen contents of organic nitrates such as the nitro-celluloses.

AQUA-REGIA.

311 This name is given to a mixture of nitric and hydrochloric acids which is frequently employed for dissolving the noble metals, such as gold and platinum, as well as many metallic ores and other bodies. A method of preparing this substance was described by the Latin Geber in his work, *De Inventione Veritatis*, by dissolving sal-ammoniac in nitric acid; and he states that the liquid thus obtained has the power of dissolving gold and sulphur. The name aqua-regia is first found in the writings of "Basil Valentine." He, like Geber, prepared it by dissolving four ounces of sal-ammoniac in 1 lb. of aqua-fortis; he also states that strong aqua-regia can be obtained by

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[1] *Ber.* 1878, **11**, 434.

mixing hydrochloric and nitric acids. The solvent power of aqua-regia depends upon the fact that, on heating, this mixture of acids evolves chlorine; thus:—

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2.$$

The compound nitrosyl chloride, NOCl, which is liberated at the same time, is described on page 557.

NITROGEN PENTOXIDE, $N_2O_5 = 107{\cdot}26$.

312 This substance, which is sometimes called nitric anhydride, was discovered in 1849 by Deville,[1] who obtained it by leading perfectly dry chlorine gas over dry silver nitrate contained in a U-tube placed in a water-bath. The reaction begins at 95°, and when cooled to 60° the decomposition of the nitrate goes on regularly. The pentoxide is collected in a bulb tube surrounded by a freezing mixture. The following equation represents the reaction which takes place:—

$$4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2.$$

In the preparation of the substance all joints of cork and caoutchouc must be avoided, and the parts of the glass apparatus must be connected either by fusion, or by placing the end of one tube inside the other and closing the space between the tubes with asbestos, the pores of which are filled up with melted paraffin.

Nitrogen pentoxide can be also prepared still more simply from pure perfectly anhydrous nitric acid by withdrawal from this substance of the elements of water. For this purpose nitric acid is distilled two or three times with concentrated sulphuric acid to remove all water, and is then introduced into a retort to the neck of which a long glass tube is fused to serve as a condenser. Phosphorus pentoxide is next gradually added until the mixture has a syrupy consistency, the retort being cooled with ice-water during the addition; if the nitric acid has been properly dehydrated no hissing noise is heard on addition of the anhydride. The reaction which here takes place may be thus represented:—

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3.$$

By gently heating the retort, a deep orange-coloured distillate

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[1] *Ann. Chim. Phys.* 1850, [3], **28**, 241.

is obtained, which on standing separates out into two layers. The upper or lighter layer is then poured into a thin stoppered tube and cooled down by plunging the tube into ice-cold water. Crystals of the pentoxide soon separate out, and these may be purified by pouring off the orange-coloured liquid from which they are deposited, melting the crystals at a moderate heat, again allowing them to deposit, and finally pouring off the mother liquor. The pentoxide is also formed directly by the action of ozone on nitrogen tetroxide.[1]

Properties.—Nitrogen pentoxide is a colourless solid, crystallising in bright rhombic crystals, or in six-sided prisms derived from these. When heated to 15—20° the crystals become of a yellowish colour, and melt at about 30° to a dark yellow liquid, which decomposes between 45° and 50° with the evolution of dense brown fumes. When suddenly heated, the pentoxide decomposes with explosive violence into nitrogen peroxide and oxygen, and this sudden decomposition occurs sometimes even at ordinary temperatures, if the crystals have been kept for some time. The lower the temperature is kept the longer does the substance remain unaltered, and below 30° it may be sublimed in a closed vessel, depositing in crystals in the cool part of the tube. In dry air the pentoxide volatilises very quickly, whilst in moist air it deliquesces with formation of nitric acid. Thrown into water, it dissolves with evolution of heat, forming nitric acid; thus:—

$$\left.\begin{matrix}\mathrm{NO_2}\\\mathrm{NO_2}\end{matrix}\right\}\mathrm{O}+\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}=\left.\begin{matrix}\mathrm{NO_2}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}+\left.\begin{matrix}\mathrm{NO_2}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}.$$

The pentoxide possesses very powerful oxidising properties. Thus, if brought in contact with sulphur it forms white vapours, which condense to a white sublimate of *nitrosulphonic anhydride*, $S_2O_5(NO_2)_2$. Phosphorus and potassium burn with brilliancy in the slightly warmed anhydride. Charcoal does not decompose even the boiling anhydride, but when ignited and brought into the vapour it burns with a brilliant light. When brought in contact with nitric acid, the anhydride combines to form the compound $N_2O_5+2HNO_3$. This substance, which is a liquid at the ordinary temperature, possesses at 18° a specific gravity of 1·642, and solidifies at 5° to a crystalline mass. It forms the heavy layer obtained in the preparation of the pentoxide, and decomposes with explosion when heated.

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[1] Helbig, *Atti. R. Accad. Lincei*, 1903, [5], 12, i. 211.

NITRAMIDE, $NO_2{\cdot}NH_2$.

This substance, which is isomeric with hyponitrous acid (p. 547), has been prepared by the action of cooled sulphuric acid on potassium nitrocarbamate, $NO_2{\cdot}NK{\cdot}CO_2K$. It is an unstable compound, which crystallises in soft lustrous plates and melts and decomposes at 72°. It decomposes very readily into nitrous oxide and water with evolution of heat, when simply mixed with a fine powder, such as powdered glass, and its aqueous solution, which has an acid reaction, is at once decomposed in a similar manner by alkalis and even by sodium acetate.[1]

Some doubt has been expressed as to the constitution of this substance, and it has been suggested that it is in reality a stereoisomeride of hyponitrous acid, *i.e.*, that it has the same chemical constitution, viz., $HO{\cdot}N:N{\cdot}OH$, but that the groups are differently arranged in space.[2]

NITROGEN MONOXIDE OR NITROUS OXIDE, $N_2O = 43{\cdot}74$.

313 This gas is formed by the action of easily oxidisable substances, such as potassium sulphide, moist iron filings, the sulphites, and other bodies upon nitric oxide, and according to these methods it was first prepared by Priestley in the year 1772. It is, moreover, formed when zinc and other metals are dissolved in very dilute nitric acid, and by the action of sulphur dioxide on nitric oxide in presence of moisture.[3]

Preparation.—In order to prepare the gas we do not, however, usually employ any of these methods, but we have recourse to the decomposition which ammonium nitrate undergoes on heating. This salt splits up into water and nitrous oxide gas; thus:—

$$NH_4NO_3 = N_2O + 2H_2O.$$

It is best, before the experiment, to melt the nitrate, in order to free it from moisture, and the powdered dry substance is then introduced into a flask furnished with a cork and delivery tube. The flask must be heated gently until a regular evolution of gas begins, and then the flame moderated, as sometimes, if the

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[1] Thiele and Lachmann, *Ber.* 1894, **27**, 1909.

[2] Hantzsch and Kaufmann, *Annalen*, 1896, **292**, 317; Hantzsch, *Annalen*, 1896, **292**, 340; Baur, *Annalen*, 1897, **296**, 95.

[3] Lunge, *Ber.* 1881, **14**, 2196.

heat applied be too great, the decomposition takes place so violently, with evolution at the same time of nitric oxide, that an explosion may occur. The heating should, moreover, be discontinued while a certain amount of the nitrate remains undecomposed. In order to free the gas from traces of nitric oxide it can be shaken up with a solution of ferrous sulphate, which combines with the latter gas; whilst in order to remove traces of chlorine derived from the chloride of ammonium, which the commercial nitrate often contains, it must be allowed to stand over a solution of caustic potash or soda. These precautions are especially needed when the gas is used for inhaling. A regular stream of the gas may also be obtained by heating sodium nitrate with a slight excess of ammonium sulphate at 240°.[1]

The pure gas may also be conveniently prepared by heating at 260—285° a mixture of 2 parts of ammonium nitrate dried at 105° with 3 parts of sand, and passing the gas through a solution of sodium sulphide or ferrous sulphate, and finally through an emulsion of ferrous sulphate in concentrated sulphuric acid.[2]

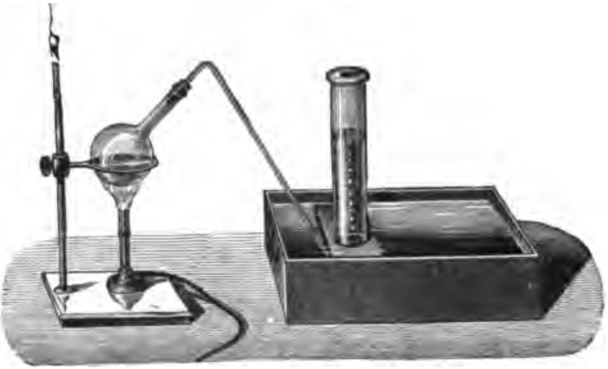

FIG. 141.

A ready method of obtaining the gas of great purity is to allow a quantity of the liquefied gas to evaporate partially and then collect the gas evolved from the residue, which is free from nitrogen.[3]

As nitrous oxide is somewhat soluble in cold, but not nearly so soluble in hot water, it is best to fill the pneumatic trough

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[1] W. Smith, *J. Chem. Soc. Ind.* 1892, **11**, 867; 1893, **12**, 10.

[2] Lidoff, *J. Russ. Chem. Soc.* 1903, **35**, 59.

[3] Villard, *Compt. Rend.* 1894, **118**, 1096.

with warm water before collecting the gas. The arrangement used for this purpose is seen in Fig. 141, and requires no further explanation.

314 *Properties.*—Under ordinary circumstances nitrogen monoxide is a colourless gas possessing a pleasant smell and sweet, agreeable taste, and having a specific gravity of 1·5297 (Rayleigh[1]), 1·5301 (Leduc[2]).

Its solubility in water between 0° and 25° is represented by the formula

$$c = 1{\cdot}30521 - 0{\cdot}045620t + 0{\cdot}0006843t^2;$$

or its coefficients of absorption are as follows:[3]—

0°	5°	10°	15°	20°	25°
1·3052	1·0954	0·9196	0·7778	0·6700	0·5962

It is still more soluble in alcohol, one volume of this liquid absorbing, according to the experiments of Carius, a quantity of the gas found by the formula

$$c = 4{\cdot}17805 - 0{\cdot}0698160t + 0{\cdot}0006090t^2.$$

Nitrous oxide was first liquefied by Faraday in 1823 by heating nitrate of ammonium in a bent tube. The liquid is now prepared on the manufacturing scale by compressing the gas into strong cylinders; it is a colourless very mobile liquid, which has a specific gravity at 0° of 0·9369 (Andreef[4]), 0·9105 (Villard), boils at −89·8° and freezes at −103·7° (Ramsay and Shields[5]). Its critical temperature is 37° (Cailletet and Mathias[6]), 38·8° (Villard[7]), its critical pressure 77·5 atmospheres, and its critical volume 0·00436. For experimental purposes the liquid may be transferred to open vessels by placing the cylinder with the valve downwards, and carefully opening the latter, the liquid rushing out in a fine stream through the nozzle.

Like other condensed gases, liquid nitrous oxide has a very high coefficient of expansion; one volume of the liquid at 0° becoming 1·1202 volumes at 20°, whereas one volume of the gas at 0° becomes only 1·0732 volumes when raised to 20°. Phosphorus,

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[1] *Proc. Roy. Soc.* 1897, **62**, 204; *Nature*, 1904, **70**, 523.

[2] *Compt. Rend.* 1897, **125**, 571.

[3] Carius, *Annalen*, 1855, **94**, 140. See also Roth, *Zeit. physikal. Chem.* 1897, **24**, 114.

[4] Andreef, *Annalen*, 1858, **110**, 11.

[5] *Journ. Chem. Soc.* 1893, 135.

[6] *Journ. de Physique*, 1886, [2], **5**, 549.

[7] *Compt. Rend.* 1894, **118**, 1096.

potassium and charcoal do not undergo any change when thrown into liquid nitrous oxide. If a piece of burning charcoal be thrown on the liquid, it swims on the surface and continues to burn with great brilliancy; on pouring a little mercury into the tube containing the liquid nitrous oxide, the metal solidifies, whilst at the same moment the piece of ignited charcoal may be seen to be burning brilliantly on the surface of the liquid.

When liquid nitrous oxide is poured into carbon bisulphide the two liquids mix, and if the mixture be brought under the receiver of an air-pump the temperature sinks to $-140°$.

Solid nitrous oxide in the form of snow has also been prepared by Wills,[1] who obtained it by a modification of Thilorier's method of obtaining solid carbon dioxide.

Gaseous nitrous oxide, like oxygen, supports combustion vigorously. A red-hot splinter of wood rekindles when brought into the gas, a watch-spring burns with bright scintillations, and a bright flame of sulphur continues to burn with a brighter flame. If, however, the sulphur be only just kindled, the flame is extinguished on bringing it into the gas, as then the temperature of the flame is not sufficiently high to decompose the gas into its constituents. All combustions in this gas are simply combustions in oxygen, the burning body not uniting with the nitrous oxide, but with its oxygen, the nitrogen being liberated.

Potassium and sodium also burn brightly in the gas when slightly heated, with formation of the peroxides of these metals, and these again when more strongly ignited in the gas yield the nitrites of the metals.

Strongly heated copper decomposes the gas quantitatively:

$$N_2O + Cu = N_2 + CuO.$$

At lower temperatures nitrous oxide often produces less complete oxidation than oxygen or air at the same temperature. Thus copper is converted into cuprous oxide, Cu_2O, below 350°, but not into cupric oxide,[2] and potassium yields an oxide, K_2O_3, which spontaneously absorbs oxygen when it is brought into the air.[3] Nitrous oxide is formed from its elements with absorption of heat (p. 252), and like many substances of this class decomposes

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[1] *Journ. Chem. Soc.* 1874, 21.

[2] Sabatier and Senderens, *Compt. Rend.* 1895, **120**, 618.

[3] Holt and Sims, *Journ. Chem. Soc.* 1894, 438.

explosively into its elements when subjected to a violent shock, such as that caused by the detonation of a small charge of mercury fulminate.[1]

It unites with water at a low temperature forming an unstable crystalline hydrate,[2] $N_2O + 6H_2O$.

The very remarkable effects on the organism produced by the inhalation of nitrous oxide, first observed by Davy, have been further investigated by Hermann.[3] The first effects noticed are singing in the ears, then insensibility, and, if the inhalation be continued, death through suffocation. In the case of small animals, such as birds, fatal effects are observed in 30 seconds, and in rabbits after the expiration of a few minutes. If, however, air be again allowed to enter the lungs as soon as insensibility has set in, the effects quickly pass away and no serious results follow. When a mixture of four volumes of this gas and one volume of oxygen is breathed for from one-and-a-half to two minutes, a curious kind of nervous excitement or transient intoxication is produced, without loss ot consciousness, and this soon passes off without leaving any evil consequences. Hence this substance received the name of laughing-gas. Nitrous oxide is now largely employed as an anæsthetic agent instead of chloroform in cases of slight surgical operations, especially in dentistry, where only a short period of unconsciousness is needed. Care must, however, be taken that for these purposes the gas is free from chlorine and nitric oxide.

The composition of nitrous oxide may be ascertained in various ways; thus, a given volume of the gas is brought into a bent glass tube over mercury in the upper part of which a small piece of sodium is placed. The lower and open end of the tube is then closed under the mercury by the finger, and the part of the tube containing the sodium heated with a lamp. After the combustion, the tube is allowed to cool, and the volume of the residual gas measured. This is found to be the same as the original volume taken, and to consist entirely of nitrogen. Now, as 22·25 litres of nitrous oxide are found by experiment to weigh 43·74 grams, and 22·25 litres of nitrogen are known to weigh 27·86 grams, it is clear that the difference, or 15·88, is due to the oxygen. Hence we see that the molecule

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[1] Maquenne, *Compt. Rend.* 1895, **121**, 424.

[2] Villard, *Compt. Rend.* 1888, **106**, 1602; 1894, **118**, 646.

[3] *Jahresbericht*, 1865, 662.

of nitrous oxide consists of two atoms of nitrogen combined with one of oxygen.

The same result is attained when a spiral of steel wire is placed in a given volume of the gas and heated to redness by an electric current. The iron then burns in the gas, and a volume of nitrogen remains, equal to that of the nitrous oxide employed.

By means of eudiometric analysis we may likewise determine the composition of the gas, and for this purpose the nitrous oxide must be mixed with hydrogen and the mixture exploded by an electric spark, when water is formed and nitrogen gas is left behind; thus:—

$$N_2O + H_2 = N_2 + H_2O.$$

It can also be exploded with moist carbon monoxide.

HYPONITROUS ACID, $H_2N_2O_2$.

315 The salts of this acid were first obtained by Divers[1] by the reduction of an aqueous solution of potassium nitrate with sodium amalgam; the first product of the reaction is potassium nitrite, which on further reduction yields, in addition to some hydroxylamine, potassium hyponitrite, which is found[2] to have the empirical composition KNO. It is also obtained by the electrolysis of a solution of potassium nitrite,[3] by the action of ferrous hydroxide on a nitrite, and by the action of nitric oxide on alkaline ferrous or stannous hydroxides,[4] and is always isolated by the addition of silver nitrate which yields silver hyponitrite as a yellow precipitate.

The salts are best prepared from pure sodium nitrite either by reduction, which yields about one-sixth of the equivalent, or by conversion into sodium hydroxylaminesulphonate, $HO.NH.SO_3Na$ (p. 569), followed by the hydrolysis of this by an alkali, a process which yields 60 per cent. of the theoretical amount. It has already been stated that dilute acids convert this substance into hydroxylamine sulphate, but with alkalis no

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[1] See *Journ. Chem. Soc.* 1899, 97, where a bibliography of the literature is given.

[2] Divers, *Proc. Roy. Soc.* 1871, **19**, 425.

[3] Zorn, *Ber.* 1879, **12**, 1509. See also Tanatar, *Ber.* 1896, **29**, 1039.

[4] Divers and Haga, *Journ. Chem. Soc.* 1885, 561; Dunstan and Dymond, *Journ. Chem. Soc.* 1887, 646.

trace of hydroxylamine is formed, the sole products being a sulphite, a hyponitrite, and nitrous oxide, the latter being a decomposition product of the hyponitrites,[1]

$$2HO.NH.SO_3Na + 4KOH = K_2N_2O_2 + 2KNaSO_3 + 4H_2O.$$

Hyponitrous acid is further obtained by adding a solution of sodium nitrite to one of hydroxylamine sulphate and rapidly heating to 60°, the following reaction taking place:—

$$HO.NH_2 + ON.OH = HO.N:N.OH + H_2O.$$

The acid quickly splits up into nitrous oxide and water, but if silver nitrate solution be at once added a considerable quantity of silver hyponitrite is thrown down.[2]

It has also been obtained from hydroxylamine by the action of various oxidising agents, such as mercuric oxide and sodium hypobromite, and from certain organic derivatives of hydroxylamine.[3]

Free hyponitrous acid is prepared by adding silver hyponitrite to an ethereal solution of hydrochloric acid, filtering off the silver chloride, and evaporating in vacuo. It crystallises in deliquescent leaflets, which are soluble in water and alcohol, and it explodes spontaneously when preserved.[4]

An aqueous solution of hyponitrous acid may be obtained by the action of the calculated amount of dilute hydrochloric acid on the silver salt; it is colourless and acid, and decomposes into its anhydride (nitrous oxide) and water, slowly in the cold, more rapidly when heated, the decomposition being greater with more concentrated solutions. The solutions of the salts in water are alkaline, and behave in a similar manner to those of the acid.

On titration with potash in presence of either phenolphthaleïn or litmus it remains acid until the acid salt is formed and then becomes alkaline, but it does not expel carbon dioxide from the alkali carbonates. In acid solution it is converted by potassium

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[1] Divers and Haga, *Journ. Chem. Soc.* 1889, 760; 1899, 77; Divers, *Journ. Chem. Soc.* 1899, 95.

[2] Wislicenus, *Ber.* 1893, **26**, 772; Paal, *Ber.* 1893, **26**, 1026; Tanatar, *J. Russ. Chem. Ges.* **25**, 342; *Ber.* 1894, **27**, 187; Thum, *Monatsh.* 1893, **14**, 294.

[3] Kolotow, *Journ. phys. Russ.* 1890, **23**, 3; Thum, *Monatsh.* 1893, **14**, 294; Piloty, *Ber.* 1896, **29**, 1559; Hantzsch, *Ber.* 1897, **30**, 2356; Hantzsch and Sauer, *Annalen*, 1898, **299**, 67.

[4] Hantzsch and Kaufmann, *Annalen*, 1896, **292**, 317; see also Tanatar, *Ber.* 1896, **29**, 1039.

permanganate quantitatively into nitric acid, but in alkaline solution yields nitrous acid. When quite pure it neither decolorises iodine nor liberates the latter from solutions of potassium iodide (Thum).

With lead acetate solution the salts give a white precipitate which becomes dense and yellow after a time, and with silver nitrate a yellow precipitate, which dissolves in acids, but is reprecipitated by ammonia. The acid solution does not colour ferrous sulphate, but on addition of strong sulphuric acid the black coloration characteristic of nitric oxide is observed.

Hyponitrous acid and its salts are extremely stable towards reducing agents, but yield a certain amount of hydrazine when they are treated with sodium bisulphite, and then reduced with zinc and acetic acid.[1]

The formation of hyponitrites from derivatives of hydroxylamine shows that in these salts the oxygen atom must be united with both the nitrogen atom and that of the metal, N.O.K; nitrogen is, however, never known to act as a monad element, and it is, therefore, probable that the hyponitrites have the double formula

$$\begin{array}{l} \text{N.O.K} \\ \| \\ \text{N.O.K} \end{array}$$

This is further confirmed by the facts that the vapour density of ethyl hyponitrite corresponds to the formula $(C_2H_5)_2N_2O_2$,[2] and that the molecular formula of hyponitrous acid in aqueous solution has been found[3] by the cryoscopic method to be $H_2N_2O_2$.

NITRIC OXIDE, OR NITROGEN DIOXIDE, NO = 29·81.

316 This gas was first observed by Van Helmont, who included it under the term *gas sylvestre*. It was afterwards more fully investigated by Priestley, who named it nitrous air (see "Historical Introduction").

Preparation.—The gas is formed when nitric acid acts on certain metals such as copper, silver, mercury, zinc, &c., as also upon phosphorus and some other easily oxidisable substances. It is usually prepared by dissolving copper foil or copper

[1] von Brackel, *Ber.* 1900, **33**, 2115.

[2] Zorn, *Ber.* 1878, **11**, 1630.

[3] Hantzsch and Kaufmann, *Annalen*, 1896, **292**, 317.

turnings in nitric acid of specific gravity 1·2, washing the gas by passing it through water and caustic soda, and collecting it over cold water in the pneumatic trough. The reaction occurring in this case is expressed as follows:—

$$3Cu + 8HNO_3 = 2NO + 3Cu(NO_3)_2 + 4H_2O.$$

The gas thus obtained is, however, not pure, as it invariably contains free nitrogen and nitrous oxide, the quantity of the latter gas increasing with the amount of copper nitrate which is formed.[1] A purer gas may be obtained by this method by allowing the nitric acid to drop on to copper turnings and running off the copper nitrate solution which is produced.[2] In order to obtain a much purer gas the nitric oxide must be passed into a cold concentrated solution of ferrous sulphate or chloride. With this it forms a singular compound, to be described hereafter, which dissolves in water with formation of a deep blackish-brown solution. On heating this solution, nitric oxide is given off, but this gas still contains one-500th of its volume which is not absorbable by ferrous salts.[3] The gas can also be obtained almost pure by heating ferrous sulphate with nitric acid, or by heating a mixture of ferrous sulphate and sodium nitrate with dilute sulphuric acid; by allowing a concentrated solution of sodium nitrite to drop into a hydrochloric acid solution of ferrous sulphate or chloride[4] and by mixing solutions of potassium ferrocyanide, sodium nitrite and acetic acid and shaking well.[5] Pure nitric oxide may be prepared by acting on mercury with a mixture of sulphuric and nitric acids,[6] a reaction which has been made use of by Lunge in his nitrometer for the estimation of the oxides of nitrogen in sulphuric acid. It may also be obtained by the fractional distillation of the liquefied gas.

Properties.—Nitric oxide is a colourless gas having a specific gravity of 1·039 (Bérard), 1·0387 (Leduc[7]), whilst according to Gray[8] the weight of 1 litre is 1·3402 grams, and the density therefore 1·0363. It was first liquefied by Cailletet in November, 1877, by expanding the gas from a pressure of 104 atmospheres at a temperature of −11°. It boils at −149·9° (Ramsay and

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[1] Ackworth, *Journ. Chem. Soc.* 1875, 828.

[2] Senier, *Proc. Chem. Soc.* 1900, 227.

[3] Leduc, *Compt. Rend.* 1893, **116**, 323.

[4] Thiele, *Annalen*, 1889, **253**, 246.

[5] Deventer, *Ber.* 1893, **26**, 589.

[6] Emich, *Monatsh.* 1892, **13**, 73.

[7] *Compt. Rend.* 1893, **116**, 322

[8] *Proc. Chem. Soc.* 1903, 66.

Travers), −153·6° (Olszewski[1]), and has the critical temperature −93·5°. It forms a colourless liquid, which is rendered blue by a minute trace of a higher oxide (Travers[2]), whereas according to Dewar[3] the liquid is blue and the solid colourless. When mixed with an excess of oxygen it yields almost entirely nitrogen peroxide, but, according to Lunge, when nitric oxide is in excess, nitrogen trioxide is also formed; with an excess of oxygen and moisture it is chiefly converted into nitric acid, whilst with even an excess of oxygen in presence of concentrated sulphuric acid it yields solely nitrosylsulphuric acid (p. 564.), and no nitrogen peroxide or nitric acid.[4] On exposure to air, this gas at once combines with the atmospheric oxygen, with evolution of heat and formation of red fumes of higher oxides. No combination occurs when the perfectly dry gas is mixed with dry oxygen.[5] Solid nitric oxide combines explosively with liquid oxygen, unless the mixture be carefully cooled by complete immersion in liquid oxygen.[6]

Nitric oxide is extremely stable when heated, decomposition commencing at a faint red heat, but being very slight at 900°, and not being complete until the temperature of melted platinum (1775°) is reached.[7] Its formation from its elements is attended by absorption of heat (p. 252), and when exposed to the shock from an explosion of mercury fulminate,[8] it is resolved into its elements.

If a spiral of iron wire be heated to redness in this gas by means of an electric current, the iron burns brilliantly so long as any nitric oxide remains undecomposed, and after the combustion the residual gas is found to consist of nitrogen exactly equal in volume to one-half of the gas employed. A mixture of the gas with hydrogen does not explode when a spark is passed through it, but complete combustion occurs when it is slowly passed through a heated capillary tube of platinum,[9] or over finely divided nickel[10] or copper above 180°.

When a stream of the gas is passed over heated potassium

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[1] Olszewski, *Compt. Rend.* 1885, **100**, 940.

[2] *Experimental Studies of Gases* (1901) p. 244.

[3] *Proc. Chem. Soc.* 1895, 225.

[4] *Ber.* 1885, **18**, 1384.

[5] Baker, *Journ. Chem. Soc.* 1894, 613.

[6] Dewar, *Proc. Chem. Soc.* 1895, 225.

[7] Emich, *Monatsh.* 1892, **13**, 78, 615.

[8] Berthelot, *Compt. Rend.* 1881, **93**, 613.

[9] Knorre and Arndt, *Ber.* 1899, **32**, 2136.

[10] Sabatier and Senderens, *Compt. Rend.* 1902, **135**, 278.

this metal takes fire and burns brilliantly, forming a mixture of nitrite and nitrate. The gas decomposes heated potassium chlorate and iodate, liberating the halogen and forming the nitrate along with nitrogen peroxide;[1] whereas metallic sodium, even when heated with a spirit-lamp, remains unaltered in the gas. Phosphorus also burns with a dazzling brilliancy in nitric oxide, but only when it is brought into the gas already brightly burning. The flame of feebly burning phosphorus, as well as that of sulphur and of a candle, are, on the other hand, extinguished on plunging them into nitric oxide, because the temperature of these flames is not sufficiently high to decompose this gas into its elementary constituents. If a few drops of carbon bisulphide be poured into a long glass cylinder filled with nitric oxide vapour, and the cylinder well shaken so that the vapour of the bisulphide is well mixed with the gas, the mixture burns with a splendid blue and intensely luminous flame, which is characterised by its richness in the violet or chemically active rays. So intense is this light in the violet and ultra-violet rays, that a lamp in which the two gases are burnt has been constructed for the use of photographers.[2] Nitric oxide is completely absorbed by a strong solution of sodium sulphite containing caustic soda, sodium hyponitrososulphate, $Na_2N_2O_2SO_3$, being formed.[3] It is partly absorbed and partly reduced to nitrous oxide by alkaline solutions of pyrogallic acid,[4] and is reduced to nitrous oxide and nitrogen by zinc or iron.[5]

The name nitrogen dioxide was given to this gas because for the same quantity of nitrogen it contains twice as much oxygen as nitrous oxide or nitrogen monoxide. Its relative density, however, which remains constant down to $-70°$,[6] is about 15, and the gas has therefore the formula NO, and consequently possesses a simpler constitution than nitrous oxide. The chemical and physical properties of nitric oxide bear out this view. Thus, it does not condense under circumstances which effect the liquefaction of nitrous oxide; it is also much more stable than this latter gas, so that it follows a law which we find to hold good with regard to analogous gaseous bodies, viz., that those possessing the simpler constitution are, as a rule, much less easily con-

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[1] Fowler and Auden, *Chem. News.* 1895, **72**, 163.

[2] Sell, *Ber.* 1874, **7**, 1522.

[3] Divers, *Journ. Chem. Soc.* 1899, 92.

[4] Oppenheimer, *Ber.* 1903, **36**, 1744.

[5] Sabatier and Senderens, *Compt. Rend.* 1895, **120**, 1158.

[6] Daccomo and V. Meyer, *Annalen*, 1887, **240**, 326.

densable, and much less easily decomposable, than those of more complicated constitution.

317 *Nitrohydroxylamic acid,* $H_2N_2O_3$.—The sodium salt, $Na_2N_2O_3$, of this unstable acid is formed when methyl nitrate, CH_3NO_3, is added to a solution of free hydroxylamine and caustic soda in methyl alcohol, and is a white powder which is extremely soluble in water. The solution rapidly absorbs oxygen from the air, sodium nitrite and nitrate being produced, and when it is boiled the salt decomposes according to the equation:

$$2Na_2N_2O_3 + H_2O = 2NaNO_2 + N_2O + 2NaOH.$$

When the solid salt is gently heated, on the other hand, it decomposes into sodium nitrite and hyponitrite.

The addition of a mineral acid to the aqueous solution produces a vigorous effervescence, the free acid decomposing at once into nitric oxide and water:

$$H_2N_2O_3 = 2NO + H_2O.$$

The barium salt is an insoluble white powder, and the silver salt an unstable yellow precipitate.

This acid has the composition of a hydrate of nitric oxide, and, as we have seen, it actually decomposes into this gas and water as soon as it is liberated. Its reactions both with inorganic and organic substances point to the constitution $HO.N{:}NO_2H$.[1]

NITROGEN TRIOXIDE OR NITROUS ANHYDRIDE, $N_2O_3 = 75{\cdot}50$.

318 When starch, sugar, arsenious anhydride and other easily oxidisable bodies are heated with nitric acid, red fumes are given off, the composition of which varies with the strength of the acid employed. When arsenious oxide is acted on by nitric acid of specific gravity 1·35, or starch by an acid of specific gravity 1·33,[2] the gas which is evolved has almost the empirical composition of nitrous anhydride, N_2O_3, and behaves in many reactions as though it were this substance. Thus it is completely absorbed by sulphuric acid, forming nitrosyl-sulphuric acid (p. 564), reacts with aromatic amino-compounds to form diazo-com-

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[1] Angeli, *Gazzetta*, 1896, **26**, ii. 17; 1897, **27**, ii. 357; *Real. Accad. Lincei*, 1901, [5], **10**, ii. 158. Angeli and Angelico, *Gazzetta*, 1900, **30**, i. 593; 1903, **33**, ii. 245; *Real. Accad. Lincei*, 1901, [5], **10**, i. 249. Angelico and Fanara, *Gazzetta*, 1901, **31**, ii. 15.

[2] Lunge, *Ber.* 1878, **11**, 1641.

pounds (Vol. III., Pt. iii., 1891, p. 26), and is absorbed by caustic soda solution with formation of pure sodium nitrite.[1] In spite of this, however, many facts show that these red fumes consist mainly of a mixture of nitric oxide with nitrogen peroxide. The vapour density of the gas corresponds with this supposition, and no contraction occurs when nitric oxide and nitrogen peroxide are mixed.[2] It has, however, been shown by Dixon and Peterkin[3] that nitrogen peroxide undergoes an expansion of about 6 per cent. when it is mixed with an equal volume of nitrogen at 27°. This is due to the fact that the peroxide at 27° is a mixture of molecules of N_2O_4 with the simpler molecules NO_2 (p. 560), and that when the partial pressure of the gas is lowered by admixture with an indifferent gas, the dissociation is increased and an increase of volume results. When nitrogen peroxide is mixed with nitric oxide at 27°, however, no expansion occurs, but a very slight contraction is observed. It follows from this that, after mixing, about 3 per cent. of the gas is present in the form of nitrogen trioxide. The presence of this small amount of trioxide in the gas explains its behaviour to reagents, since the removal of the trioxide from the mixture would disturb the equilibrium, a fresh amount would be formed and removed, and in this way the whole of the gas might react as the trioxide.

Nitrogen trioxide is formed when electric discharges are passed through liquid air.[4] A greenish flocculent precipitate is thus produced, which resembles precipitated chromium hydroxide, and is left as a pale blue amorphous powder, when the air is removed by evaporation. It melts at $-111°$ to a deep blue liquid, and commences to decompose above this temperature; the blue liquid solidifies when cooled to a deep blue solid. The composition of solid nitrogen trioxide was determined by passing the gases evolved by its decomposition over heated copper and estimating the amount of free nitrogen produced and of copper oxide formed. A deep blue liquid is also obtained by the condensation of the red fumes evolved by the action of nitric acid on starch. It is also produced by the direct union of nitric oxide with solid nitrogen peroxide[5] and of

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[1] Divers, *Journ. Chem. Soc.* 1899, 86.

[2] Witt, *Ber.* 1878, **11**, 756; 1879, **12**, 2188; Ramsay and Cundall, *Journ. Chem. Soc.* 1885, 187, 672; Geuther, *Annalen*, 1888, **245**, 96; Lunge and Porschnew, *Zeit. anorg. Chem.* 1894, **7**, 209.

[3] *Journ. Chem. Soc.* 1899, 614.

[4] Helbig, *Atti. R. Accad. Lincei*, 1902, [5], **11**, ii. 57; 1903, [5], **12**, i. 166.

[5] von Wittorff, *Zeit. anorg. Chem.*, 1904, **41**, 85.

oxygen with liquid nitric oxide, and is not converted by oxygen into the peroxide below −100°.[1]

It seems probable that this oxide is the first product of the action of the spark on air, as was suggested by Berthelot from the fact that when a mixture of nitrogen and oxygen is sparked over caustic soda more nitrite than nitrate is produced.[2]

Nitrous Acid, HNO_2.

319 Nitrogen trioxide dissolves in ice-cold water, giving rise to a beautiful blue liquid, which contains nitrous acid, as shown in the following equation:—

$$\left.\begin{matrix}NO\\NO\end{matrix}\right\}O+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}NO\\H\end{matrix}\right\}O+\left.\begin{matrix}NO\\H\end{matrix}\right\}O.$$

Nitrous acid is not known in the pure state, it being a very unstable substance, which even in aqueous solution rapidly undergoes decomposition when warmed, giving rise to nitric acid and nitric oxide gas; thus:—

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

This reaction is, however, according to Veley, a reversible one, nitric oxide yielding with nitric acid and water a small quantity of nitrous acid, the condition of equilibrium being reached when about nine molecules of nitric acid are present to one of nitrous acid.[3] The salts of this acid, or the *nitrites*, are, on the contrary, very stable bodies. They are not only formed by the action of the acid upon oxides, but also by the reduction of nitrates and by the oxidation of ammonia. Thus, for instance, potassium nitrite, KNO_2, is formed either by fusing saltpetre, or, more easily, by heating this salt with lead or copper; thus:—

$$2KNO_3 = 2KNO_2 + O_2.$$

It is also formed to some extent by the action of sunlight on a sterilised solution of potassium nitrate.[4] Nitrites also occur in nature. Thus the atmosphere contains small quantities of ammonium nitrite, and traces of nitrites have been detected in

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[1] Francesconi and Sciacca, *Gazzetta*, 1904, **34**, i. 447.

[2] *Compt. Rend.* 1899, **129**, 137.

[3] *Proc. Roy. Soc.* 1892, **52**, 27.

[4] Laurent, *Bull. Acad. Belg.* 1891, [3], **21**, 337.

the juices of certain plants (Schönbein[1]). All the normal nitrites are soluble in water, and most of them soluble in alcohol. The silver salt is the nitrite which is most sparingly soluble in cold water, crystallising out in long glittering needle-shaped crystals when the hot aqueous solution is cooled.

When sodium nitrite is reduced by sodium amalgam, nitrogen and ammonia are the chief products, when the solution is hot; in the cold, nitrous oxide, hydroxylamine, and hyponitrous acid are formed, the relative amounts varying with the concentration.[2]

The nitrites deflagrate when thrown on to glowing carbon, as do the nitrates. They can, however, be distinguished from the latter salts by the action of dilute acids, which produce an evolution of red fumes from the nitrites but not from the nitrates. In a similar way aqueous solutions of the neutral nitrites become of a light brown colour when mixed with a solution of ferrous sulphate, and this colour deepens to a dark brown on the addition of acetic acid. In order to detect the presence of a nitrite in dilute solution in the absence of other oxidising agents, iodide of potassium, starch paste, and dilute sulphuric acid are added. The latter acid sets free the nitrous acid, and this instantly decomposes the iodide with liberation of iodine.

Nitrous acid is quantitatively oxidised by potassium permanganate and by hydrogen peroxide[3] to form nitric acid, and is reduced to ammonia by boiling with ferrous sulphate and caustic soda.[4] It may be estimated by any of these methods and also by its action on urea, which it oxidises to nitrogen, carbon dioxide, and water. The free acid can, moreover, be titrated with caustic soda in dilute solution with methyl orange as indicator.[5]

Small amounts of nitrous acid or nitrites, such as occur in water, are usually detected and estimated colorimetrically. Several reagents may be employed for this purpose, such as metadiamido-benzene, which in presence of hydrochloric or sulphuric acid gives a brown coloration (Griess), or a solution of sulphanilic acid and α-naphthylamine in dilute acetic acid, which gives an intense pink coloration (Ilosvay).

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[1] See also Defren, *Chem. News*, 1896, **74**, 230, 240.

[2] Divers, *Journ. Chem. Soc.* 1899, 87.

[3] Baeyer and Villiger, *Ber.* 1901, **34**, 755.

[4] Suler, *Zeit. Elektrochem.* 1901, **7**, 831, 847.

[5] Lunge, *Zeit. angew. Chem.* 1903, **16**, 509.

The constitution of nitrous acid is not definitely known; some of the reactions undergone by both the acid and its salts point to the formula HO·NO, and others to the formula $H·NO_2$.

NITROSYL CHLORIDE, NOCl. = 64·99.

320 This chloride of nitrous acid is formed by the direct union of nitric oxide and chlorine, as well as by the action of phosphorus pentachloride upon potassium nitrite, thus:—

$$PCl_5 + NOOK = NOCl + KCl + POCl_3.$$

It is likewise formed together with free chlorine when a mixture of hydrochloric and nitric acids, the so-called *aqua regia*, is slowly heated; thus:—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

In order to obtain the chloride in the pure state, a mixture of one volume of nitric acid of specific gravity 1·42 and four volumes of hydrochloric acid of specific gravity 1·16 is gently warmed, the gases which are evolved being first dried by passing through a chloride of calcium tube, and then led into strong sulphuric acid. The chlorine and hydrochloric acid gases thus escape, whilst nitrosyl-sulphuric acid, $SO_4H(NO)$, a body to be described later on, is formed. As soon as the sulphuric acid is saturated, the liquid is heated with an excess of perfectly dry sodium chloride, when nitrosyl chloride is evolved;[1] thus:—

$$SO_2\begin{cases}ONO\\OH\end{cases} + NaCl = SO_2\begin{cases}ONa\\OH\end{cases} + NOCl.$$

It may also be prepared by passing a mixture of nitric oxide and chlorine over dry animal charcoal at 40–50°.

Nitrosyl chloride is an orange-yellow gas, the colour of which is quite different from that of chlorine. It liquefies readily when passed through a tube surrounded by a freezing mixture, forming a ruby-red liquid, which has the critical temperature 163°, boils at −5·6° at 751 mm. pressure, and solidifies to a lemon-yellow crystalline mass, melting at −60°.[2] This substance combines with many metallic chlorides, forming peculiar compounds,

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[1] Tilden, *Journ. Chem. Soc.* 1860, 630.

[2] Francesconi and Bresciani, *Atti. R. Accad. Lincei.* 1903, [5], **12**, ii. 75.

whilst, brought into contact with basic oxides, it is decomposed with formation of a nitrite and chloride; thus:—

$$NOCl + 2KOH = KNO_2 + KCl + H_2O.$$

NITROSYL BROMIDE, $NOBr. = 109{\cdot}17$.

321 In order to prepare this compound, nitric oxide is led into bromine at a temperature of −7° to −15° as long as it is absorbed. In this way a blackish-brown liquid is obtained, which begins to decompose at the temperature of −2°, nitric oxide being evolved. If the temperature is allowed to rise to + 20°, a dark brownish-red liquid remains behind which has the composition $NOBr_3$; and this is also formed when bromine is saturated with nitric oxide at the ordinary atmospheric temperature. *Nitrosyl tribromide*, $NOBr_3$, is volatilised when quickly heated, almost without decomposition, but if it is slowly distilled it decomposes into its constituents (Landolt).

NITROGEN TETROXIDE, OR NITROGEN PEROXIDE, N_2O_4, OR NO_2.

322 The red fumes which are formed when nitric oxide comes into contact with oxygen or air, consist chiefly of nitrogen peroxide. If one volume of dry oxygen be mixed with two volumes of dry nitric oxide and the red fumes which are produced led into a tube surrounded by a freezing mixture, the peroxide condenses in the tube either as a liquid or in the form of crystals.

Nitrogen peroxide is also formed by the decomposition which many nitrates undergo when heated, and is usually prepared by strongly heating lead nitrate in a retort of hard glass as shown in Fig. 142, when the following decomposition occurs:—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

This mode of preparation is, however, not very convenient, and a considerable loss of material occurs, as the oxygen which is evolved carries away some quantity of the peroxide even when the tube into which the fumes are led is plunged into a freezing mixture.

The following method is free from the above objections; arsenious oxide (white arsenic) in the form of small lumps is placed in a flask and covered with ordinary nitric acid, or, according to Cundall,[1] with a mixture of nitric acid of specific gravity 1·5 and half its weight of sulphuric acid; the red fumes, which are given off in quantity on gently heating, are led into a receiver surrounded by a freezing mixture, where a mixture of trioxide and tetroxide of nitrogen collects. The mixture is freed from the trioxide by the addition of strong nitric acid and a large quantity of phosphorus pentoxide, and the tetroxide is then poured off from the syrupy layer, and distilled. The trioxide may also be converted into peroxide by a current of air.[2]

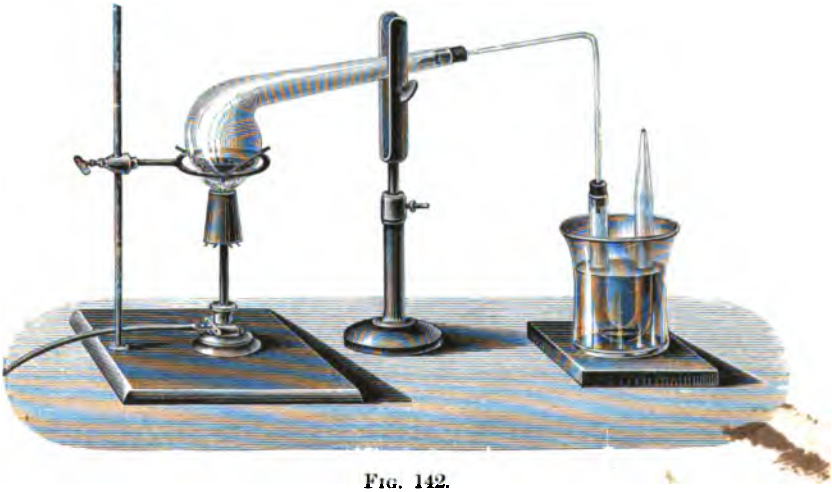

FIG. 142.

Nitrogen peroxide may also be prepared by mixing the fumes obtained by the action of nitric acid of specific gravity 1·4 on arsenious oxide with oxygen, drying over calcium nitrate, condensing and redistilling.[3]

323 *Properties.*—Nitrogen tetroxide is a liquid at the ordinary atmospheric temperatures: at −10°·1 it solidifies to a mass of colourless crystals. Slightly above this temperature the liquid compound is also colourless, but when warmed further, it

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[1] *Journ. Chem. Soc.* 1891, 1076.
[2] Frankland and Evans, *Journ. Chem. Soc.* 1901, 1356.
[3] Cohen and Calvert, *Journ. Chem. Soc.* 1897, 1052.

first becomes of a pale greenish yellow, then at +10° it attains a decided yellow colour, whilst at 15° it becomes orange-coloured, and at higher temperatures it assumes a still darker tint. The absorption spectrum of gaseous nitrogen tetroxide is a characteristic band spectrum which has been mapped by Brewster and Gladstone.

Liquid nitrogen tetroxide has a specific gravity of 1·49 at 0° and boils at 22°, forming a reddish-brown vapour possessing a very strong and unpleasant smell. When the temperature of the gas is raised, the colour becomes darker and darker, until at last it appears almost black and opaque. This is well shown by sealing some of the gaseous tetroxide in two wide glass tubes, and heating one for some little time in the flame of a lamp whilst the other remains at the ordinary temperature.

These remarkable changes in appearance are not accompanied by any equally striking changes in the absorption spectrum of the gas, although it is probable that the peroxide exists in two distinct forms, as indeed has been shown by the variations which its density exhibits. Thus, at low temperatures the density corresponds to the formula N_2O_4, and at higher ones to NO_2. The density of the vapour at different temperatures was found by Playfair and Wanklyn[1] to be as follows:—

Temperature.	Density. Air = 1.	Corresponding molecular weight.
97°·5	1·783	51·5
24°·5	2·520	—
11°·3	2·645	—
4°·2	2·588	74·8

The density required for the compound NO_2 is 1·585, that for the compound N_2O_4 the double of this, or 3·17. It will be seen that the numbers obtained all lie between these two, the density at the highest temperature not lying far from the lower number, whilst those found for the lower temperatures correspond more nearly to the density of the substance N_2O_4. From these facts we draw the conclusion that at low temperatures the molecule of the compound is represented by the formula N_2O_4, but that as the temperature rises a gradual change in the molecules of the gas takes place, one molecule of N_2O_4 splitting up, or becoming dissociated, into two of NO_2.

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[1] *Journ. Chem. Soc.* 1863, 156.

From Deville and Troost's[1] experiments the following percentage composition of the gas at various temperatures has been calculated:—

	NO_2.	N_2O_4.
at 26°·7	20·00	80·00
„ 60°·2	50·04	49·96
„ 100°·1	79·23	20·77
„ 135°	98·96	1·04
„ 140°	100·00	0·00

We thus see that at 140° the black vapour consists entirely of the simpler molecules NO_2. The amount of dissociation is also increased by diminishing the pressure (Vol. II. (1897), p. 118).

Liquid nitrogen peroxide when diluted with chloroform undergoes a similar dissociation, the amount of dissociation increasing with dilution and rise of temperature.[2]

Nitrogen tetroxide is decomposed by cold water with production of nitric and nitrous acids; thus:—

$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

This decomposition, however, only occurs at low temperatures and with small quantities of water. When nitrogen peroxide is added to an excess of water at the ordinary temperature, the nitrous acid is at once decomposed into nitric oxide and nitric acid; thus:—

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

If oxygen be present at the same time, this of course combines with the nitric oxide, forming nitrogen peroxide, which is again decomposed by water, and in this way the peroxide may be completely transformed into nitric acid. In order to exhibit this decomposition, as well as to show the formation of the peroxide and nitric acid, the following apparatus may be used (Fig. 143): the upper vessel, containing a little water, is filled with nitric oxide, and is connected with the lower vessel by the tube (*A*), which is drawn out to a point. This lower vessel contains water, coloured with blue litmus. If oxygen be now led slowly into the upper vessel by means of the tube (*B*), red fumes are formed, which are absorbed by the water. A vacuum

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[1] *Jahresb.* 1867, p. 177.

[2] Cundall, *Journ. Chem. Soc.* 1891, 1076; 1895, 794.

is thus produced, and the coloured water rises in the form of a fountain into the upper vessel, and becomes coloured red. If the nitric oxide be perfectly pure, and if care be taken that the oxygen is allowed to enter but slowly towards the end of the operation, the whole of the upper vessel may be filled with water.

Liquid nitrogen peroxide acts as a solvent for many substances, such as iodine, bromine and a large number of organic compounds, whilst inorganic salts are as a rule insoluble in it.[1]

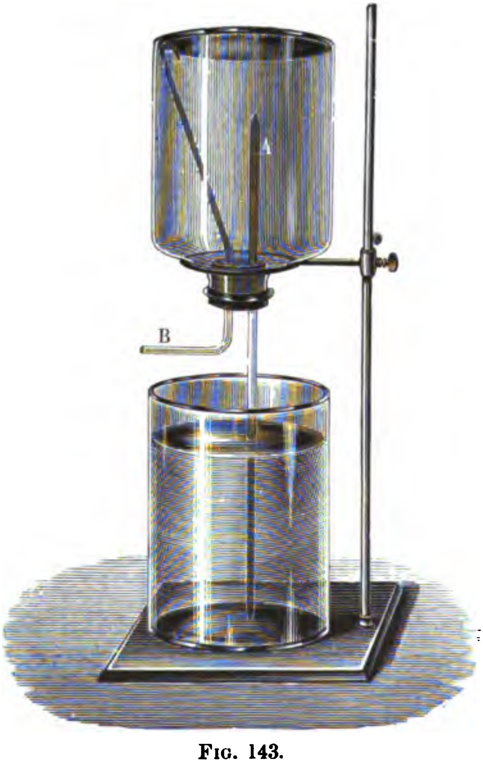

FIG. 143.

In many of its reactions nitrogen peroxide acts as a true peroxide[2] and probably has the constitution O : N.O.O.N : O. The simpler molecule formed by dissociation would then be O : N.O, in which one atom of oxygen acts as a univalent element.

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[1] Bruni and Berti, *Gazzetta*, 1900, **30**, ii, 151 ; Frankland and Evans, *Journ. Chem. Soc.* 1901, 1356.

[2] Divers, *Journ. Chem. Soc.* 1904, 110.

COMPOUNDS OF NITROGEN WITH SULPHUR AND SELENIUM.

NITROGEN SULPHIDE, N_4S_4.

324 This compound, which was discovered by Gregory in 1835, is obtained, together with other compounds, by the action of dry ammonia upon a 10–15 per cent. solution in benzene of a mixture of chlorides of sulphur which has the empirical composition SCl_2, or upon thionyl chloride. It crystallises in long orange-red rhombic prisms, has a characteristic smell and decomposes at 185° (Francis and Davis) or at 178° (Muthmann), the lower temperature being probably due to the presence of traces of free sulphur. As ordinarily prepared the compound is liable to spontaneous explosion and explodes readily on percussion. The molecular weight,[1] as determined from the freezing point of the solution in naphthalene and the boiling points of its solutions in carbon bisulphide and benzene, corresponds with the formula N_4S_4.

It is decomposed by cold water, the chief products being ammonia, sulphurous acid and thiosulphuric acid, whilst liquid hydrogen chloride produces ammonia and a mixture of the chlorides of sulphur.[2]

Nitrogen sulphide combines with chlorine to form a *tetrachloride*, $N_4S_4Cl_4$, which crystallises in golden yellow needles and is decomposed by water;[3] it unites with bromine to form a *tetra-* and a *hexa-bromide*,[4] and also forms a number of addition compounds with the chlorides of sulphur.[5]

Nitrogen sulphide reacts with sulphur monochloride or acetyl chloride to form *thio-trithiazyl chloride*, N_3S_4Cl, which acts in many respects as a salt, and is converted by nitric acid into the crystalline *nitrate*, and by bromine and iodine into the corresponding *bromide* and *iodide*, all of which are decomposed by water.[6]

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[1] A. Schenk, *Annalen*, 1896, **290**, 171; Muthmann, *Ber.* 1896, **29**, 740; Francis and Davis, *Journ. Chem. Soc.* 1904, 259.

[2] Ruff and Geisel, *Ber.* 1904, **37**, 1573, where the literature of the subject is cited.

[3] Andreocci, *Zeit. anorg. Chem.* 1897, **14**, 246.

[4] Clever and Muthmann, *Ber.* 1896, **29**, 340.

[5] Fordos and Gélis, *Compt. Rend.* 1850, **31**, 702; Demarçay, *Compt. Rend.* 1880, **91**, 854.

[6] Muthmann and Seilter, *Ber.* 1897, **30**, 627.

Little is known as to the constitution of nitrogen sulphide and its derivatives, but it is probable that all the nitrogen atoms are united with sulphur and not with each other, the formula being perhaps of the type $S:S(:N\cdot S:N)_2$.

Nitrogen pentasulphide, N_2S_5, is formed, along with other substances, when the foregoing sulphide is treated with carbon bisulphide at 100°, and appears to be a very frequent product of the decomposition of the ordinary sulphide.[1] It is a deep red liquid of specific gravity 1·901 at 18°, has a strong smell and cannot be distilled even under diminished pressure; it solidifies to a mass resembling iodine, which melts at 10–11°.

NITROSYL- AND NITRO-DERIVATIVES OF SULPHURIC ACID.

325 *Nitrosylsulphuric Acid*, $HO.SO_2.O.NO$.—This compound, which is sometimes termed nitrosulphonic acid, is commonly known as the crystals of the leaden chambers or nitrosyl sulphate, produced during the process of the manufacture of sulphuric acid whenever the supply of steam is insufficient to produce sulphuric acid. Nitrosylsulphuric acid is, however, best prepared by acting upon sulphur dioxide with concentrated nitric acid; thus:—

$$SO_2+NO_2OH=SO_2\begin{cases}OH\\O.NO.\end{cases}$$

For this purpose, dry sulphur dioxide is led into cold fuming nitric acid until the mass becomes syrupy. The semi-solid mass is then drained on a dry porous plate over sulphuric acid.

Another mode of preparing the substance is to pass the vapour of nitrosyl chloride into sulphuric acid:—

$$NOCl+SO_2\begin{cases}OH\\OH\end{cases}=SO_2\begin{cases}O.NO\\OH\end{cases}+HCl.$$

It is likewise formed when nitrogen trioxide (nitrous fumes) is brought together with sulphuric acid:

$$N_2O_3+2SO_2\begin{cases}OH\\OH\end{cases}=2SO_2\begin{cases}O.NO\\OH\end{cases}+H_2O.$$

Nitrogen peroxide also yields the same product with sulphuric acid, together with nitric acid.

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[1] Clever and Muthmann, *Zeit. anorg. Chem.* 1896, 13, 200.

The substance obtained by these reactions crystallises in four-sided rhombic prisms, or sometimes in tabular or nodular crystalline masses, which begin to melt at 30°, with evolution of vapour.

The crystals dissolve in small quantities of cold water without any evolution of gas, forming a blue liquid, which contains sulphuric and nitrous acids:

$$SO_2\begin{cases}O.NO\\OH\end{cases}+\left.\begin{matrix}H\\H\end{matrix}\right\}O=SO_2\begin{cases}OH\\OH\end{cases}+HO.NO.$$

Nitrosylsulphuric acid dissolves in concentrated sulphuric acid without decomposition, and this solution can be distilled.

Nitrosylsulphuryl Chloride, $Cl.SO_2.O.NO$.—This chloride is formed by the direct union of sulphur trioxide and nitrosyl chloride, and by the action of thionyl chloride on silver nitrate.[1] It forms a white crystalline mass, which melts on heating, with separation of nitrosyl chloride. It is decomposed in contact with water into sulphuric, hydrochloric, and nitrous acids (Weber).

Nitrosylsulphuric Anhydride, $O(SO_2.O.NO)_2$.—When nitrosylsulphuric acid is heated, it decomposes into water and this anhydride, but the latter substance cannot be obtained in a pure state in this way, as sulphuric acid is formed by the further decomposition of nitrosylsulphuric acid, and these bodies cannot be separated, since they both boil nearly at the same temperature (Michaelis).[2] It is, however, easy to obtain this anhydride by passing dry nitric oxide into sulphur trioxide, so long as it is absorbed, and warming the solution until the boiling point of the liquid is nearly reached; thus:—

$$3SO_2O+2NO=\begin{matrix}SO_2\begin{cases}ONO\\ \end{cases}\\ \quad\;\; \rangle O\\ SO_2\begin{cases}ONO.\\ \end{cases}\end{matrix}+SO_2.$$

The same compound is formed when sulphur dioxide acts upon nitrogen peroxide, as well as when the next compound to be described is heated. Nitrosylsulphuric anhydride crystallises in hard colourless quadratic prisms, melts at 217° to form a yellow liquid, becomes darker on further heating, and distils over unchanged at about 360°. The compound dissolves readily in strong sulphuric acid, forming nitrosylsulphuric acid.

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[1] Thorpe, *Journ. Chem. Soc.* 1882, 297.

[2] *Ber.* 1874, **7**, 1075.

Oxynitrosylsulphuric Anhydride, $O\left\{\begin{array}{l}SO_2.ONO\\SO_2.O.NO_2\end{array}\right.$.—When sulphur trioxide and nitrogen peroxide are brought together in the cold, the above compound separates out as a white crystalline mass, which on heating gives off oxygen, and forms the anhydride last described (Weber).

Nitroxypyrosulphuric Acid, $O(SO_2.O.NO_2)_2$.—When sulphur trioxide and nitric acid are mixed together in the cold, a thick oily liquid is formed, from which the above compound crystallises out under certain conditions of concentration. It is soluble without decomposition in warm dilute nitric acid, and, on cooling the liquid, separates out in crystals containing one molecule of water of crystallisation.

326 *Nitrososulphuric acid* (*Nitrosohydroxylaminesulphonic acid or dinitrososulphonic acid*), $H_2SN_2O_5$.—The alkali salts of this acid, which are colourless crystalline substances, are formed when nitric oxide is passed into an alkaline solution of a sulphite. The free acid is unknown, as all acids, even carbonic acid, decompose the salts into sulphates and nitrous oxide, and a similar decomposition also occurs when the salts are heated or dissolved in water, accompanied in some cases by the formation of nitric oxide and a sulphite. When reduced with sodium amalgam the salts yield a complicated mixture of hyponitrite, sulphite, sulphate, aminesulphonate and hydrazine, whilst nitrogen and nitrous oxide are evolved. Alcohol decomposes the aqueous solution in a remarkable manner, forming potassium ethyl sulphate, nitrous oxide and free caustic potash.

These results are most satisfactorily explained by the constitutional formula suggested by Divers and Haga,

$$KO.N{:}N.O.SO_3K,$$

according to which the potassium salt is derived from sulphuric acid by the substitution of the nitroso-metallic radical, KO.N:N for hydrogen.[1]

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[1] Divers and Haga, *Journ. Chem. Soc.* 1885, 203, 218; 1895, 452, 1095, 1098; 1896, 1610; Raschig, *Annalen*, 1887, **241**, 230; Hantzsch, *Ber.* 1894, **27**, 3264.

SULPHONIC ACIDS OF AMMONIA AND HYDROXYLAMINE.

327 In the year 1845 a number of crystalline salts derived from acids containing both nitrogen and sulphur were obtained by Fremy[1] by the interaction of nitrites and sulphites. He only determined their empirical formulæ, but they were further investigated by Claus,[2] who showed that they are sulphonic acids, that is, compounds containing the group SO_2OH, but wrongly regarded a number of them as sulphonic acids of the hypothetical substance NH_5.

This, however, was disproved by Berglund[3] and especially by Raschig,[4] who regarded all these compounds as sulphonic derivatives of ammonia, hydroxylamine and dihydroxylamine. Finally Divers and Haga[5] have shown that no derivatives of dihydroxylamine have been isolated and that all these compounds are actually sulphonic acid derivatives of ammonia and hydroxylamine.

It seems probable, however, that the first product of the action of sulphurous acid on nitrous acid is dihydroxylamine-sulphonic acid, $(OH)_2N.SO_3H$, or its anhydride nitrososulphonic acid, $ON.SO_3H$, (p. 569). The simplest product which can be isolated when nitrous acid is passed into a solution of sulphurous acid, a pyrosulphite or a sulphite, and when sulphur dioxide is passed into a solution of a nitrite, is, however, hydroxylamine-disulphonic acid (Divers and Haga).[6] This is formed by the sulphonation of the nitrous acid, a change which is most simply represented by the equation :—

$$HO.NO + 2H{\cdot}SO_3H = HO.N(SO_3H)_2 + H_2O.$$

Other products may then be formed from this, either by hydrolysis or by further sulphonation; thus :—

$$HO.N(SO_3H)_2 + H_2O = HO.NH.SO_3H + H_2SO_4.$$
$$HO.N(SO_3H)_2 + H.SO_3H = N(SO_3H)_3 + H_2O.$$

[1] *Annalen*, 1845, **56**, 315.
[2] *Annalen*, 1869, **152**, 336, 351; 1871, **158**, 52, 191.
[3] Lunds *Universitas Arskrift*, **12** and **13**.
[4] *Annalen*, 1887, **241**, 161.
[5] *Journ. Chem. Soc.* 1900, 432.
[6] *Journ. Chem. Soc.*, 1900, 673.

No reaction occurs between a nitrite and a normal sulphite, while the actual product obtained by the action of an acid sulphite on a nitrite depends on the conditions of the experiment, the base present serving to protect the products from furthur action.

In accordance with this view, the compounds of this class are here formulated and named, as far as possible, as derivatives of ammonia (amine) and hydroxylamine. In many cases the substances described have at various times received different names, which express different views as to their constitution, and where necessary these are also given. Thus, for example, hydroxylaminedisulphonic acid, $HO.N(SO_3H)_2$, is also known as oximidosulphonic acid.

The free acids are, as a rule, unstable and have not in every case been isolated, but the salts are well defined compounds.

The final result of the reaction between sulphurous and nitrous acids is the complete oxidation of the former to sulphuric acid, so that all these substances must be regarded as intermediate compounds.

Hydroxylaminedisulphonic acid, $HO.N(SO_3H)_2$, (*Oximidosulphonic acid*; *Sulphazotic acid* of Fremy). This acid is not known in the free state, but its potassium salt may be readily prepared by the action of potassium nitrite on potassium metasulphite, $K_2S_2O_5$,[1] at 0°;

$$2KNO_2 + 3K_2S_2O_5 + H_2O = 2HO.N(SO_3K)_2 + 2K_2SO_3.$$

The conversion of two-thirds of the neutral metasulphite in this reaction into normal sulphite, which is strongly alkaline in aqueous solution, led to the erroneous idea that free caustic potash was produced.

The same salt can also be obtained by the direct action of sulphur dioxide on a solution containing molecular proportions of potassium nitrite and potassium bicarbonate or caustic potash.

The sodium salts may be prepared in a similar manner, but are more soluble.

Potassium hydroxylaminedisulphonate, $HO.N(SO_3K)_2$, crystallises in hard rhombic prisms, which are very slightly soluble in water; when boiled with the latter or with acids it is first converted into hydroxylaminesulphonic acid and then into hydroxylamine, which combines with the sulphuric acid simul-

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[1] Divers and Haga, *Journ. Chem. Soc.* 1894, 523.

taneously produced to form the sulphate. This method is now employed for the preparation of hydroxylamine (p. 513).

Normal salts of the acid are also known, such as $KO.N(SO_3K)_2$, which are strongly alkaline in aqueous solution. All the salts are converted by boiling with concentrated caustic alkalis into a mixture of nitrite and sulphite:—

$$KO.N(SO_3K)_2 + 2KOH = H_2O + KNO_2 + 2K_2SO_3.$$

Potassium nitritohydroxylaminedisulphonate,

$$KNO_2,HO.N(SO_3K)_2,$$

is formed when the potassium salt is dissolved at 70° in a 22 per cent. solution of potassium nitrite and allowed to cool. This crystalline salt was regarded by Raschig, who obtained it indirectly by the sulphonation of potassium nitrite, as a derivative of dihydroxylaminesulphonic acid, $(HO)_2N.SO_3H$, but it is most probably simply a double salt of the foregoing composition.[1] Fremy obtained a large number of different sulphazotised salts, many of which, like the foregoing, are double salts.[2]

Hydroxylaminesulphonic acid, $HO.NH.SO_3H$, like aminesulphonic acid, is stable in the free state and forms a syrupy liquid. The *potassium* salt, $HO.NH.SO_3K$, is best obtained by the partial hydrolysis of the disulphonate with hot water, and may be purified by quick recrystallisation from that liquid. When treated with alkalis it yields salts of hyponitrous acid (p. 547), whilst acids convert it into hydroxylamine.

Dihydroxylaminesulphonic acid, $(HO)_2N.SO_3H$, or its anhydride, *nitrososulphonic acid*, $ON.SO_3H$, is believed by Raschig[3] to be formed by the direct interaction of sulphurous and nitrous acids, and to play an important part in the production of sulphuric acid by the chamber process. Neither the free acids nor any of their salts have been isolated and it seems probable that the acid is very readily decomposed into sulphuric acid and the group, NOH, known as nitroxyl.

Potassium aminetrisulphonate (*nitrilosulphonate*), $N(SO_3K)_3 + 2H_2O$.—This compound, which was termed by Fremy potassium trisulphammonate, is obtained by adding an excess of a concentrated neutral solution of potassium sulphite to a similar solution of potassium nitrite, and separates out as a crystalline precipitate

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[1] Divers and Haga, *Journ. Chem. Soc.* 1900, 432.

[2] Divers and Haga, *Journ. Chem. Soc.* 1900, 440.

[3] *Zeit. angew. Chem.* 1904, **13**, 1398.

which may be recrystallised from alkaline solution. The reaction which takes place may be represented as follows:[1]—

$$KNO_2+2K_2S_2O_5=N(SO_3K)_3+K_2SO_3.$$

It may also be prepared by passing sulphur dioxide into a mixture of potassium nitrite and caustic potash.

Potassium aminetrisulphonate crystallises with 2 mols. H_2O, and forms thin silky rhombic needles, which are decomposed in the following manner by boiling water:—

$$N(SO_3K)_3+2H_2O=NH_2SO_3H+K_2SO_4+KHSO_4.$$

Hence only two-thirds of the sulphur is precipitated as barium sulphate on adding barium chloride to the hot solution, aminesulphonic acid, which will be subsequently described, not being affected by barium chloride.

The ammonium and sodium salts are also crystalline.

Potassium aminedisulphonate (*imidodisulphonate*), $NH(SO_3K)_2$.—When the aminetrisulphonate is boiled for only a short time with water, the reaction does not proceed so far as shown in the above equation, the chief product being potassium aminedisulphonate:—

$$N(SO_3K)_3+H_2O=NH(SO_3K)_2+KHSO_4.$$

This is more readily obtained by moistening the aminetrisulphonate with dilute sulphuric acid, allowing to stand for a day, and recrystallising from dilute ammonia. It forms monoclinic crystals, and is decomposed by boiling water into aminesulphonic acid and potassium sulphate.

A large number of other aminedisulphonates have been prepared by Divers and Haga;[2] the most interesting of these are *ammonium aminedisulphonate*, $NH(SO_3NH_4)_2$, and *basic ammonium aminedisulphonate*, $NH_4.N(SO_3NH_4)_2$, which were first prepared by Rose in 1834 by the action of ammonia on sulphur trioxide and termed *parasulphatammon* and *sulphatammon* respectively.

Free aminedisulphonic acid has only been obtained in aqueous solution.

Aminesulphonic acid (*amidosulphonic acid*), $NH_2{\cdot}SO_3H$.—This

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[1] Divers and Haga, *Journ. Chem Soc.* 1901, 1093.

[2] *Annalen*, 1887, **241**, 232.

acid is, as already mentioned, the final product of the action of boiling water on the salts just described and is also formed by the direct action of sulphur dioxide on a salt of hydroxylamine (Raschig).[1] It is a very stable compound sparingly soluble in water and is a strong acid.[2] It crystallises in colourless rhombic plates, and melts and decomposes at 205°, ammonium sulphate and aminedisulphonate being first produced. The *potassium* salt, $NH_2{\cdot}SO_3K$, crystallises in very similar forms.

Hydroxylaminetrisulphonic acid, $(SO_3H)_2N.O.SO_3H$.—When a warm solution of potassium hydroxylaminedisulphonate is shaken with silver oxide or lead dioxide, a bluish violet coloration is produced, which disappears if the treatment with the oxide be continued at a higher temperature.[3] The solution then contains potassium nitrite and *potassium hydroxylaminetrisulphonate.* This salt is very readily hydrolysed to hydroxylamine and potassium hydrogen sulphate, whilst it is converted by reduction into the potassium salts of sulphuric acid and aminedisulphonic acid.

The violet coloured solution referred to above deposits golden yellow needles of an unstable salt which is probably *potassium peroxylaminesulphonate*, $(SO_3K)_2{:}N.O.O.N{:}(SO_3K)_2$.

The free acid corresponding with this salt is probably present in the "purple" acid produced by the action of sulphur dioxide on nitrosylsulphuric acid.[4]

This substance is regarded by many chemists as nitrosodisulphonic acid, $NO(SO_3H)_2$, and, as already mentioned (p. 407), is supposed to play some part in the production of sulphuric acid by the chamber process.[5]

AMIDES AND IMIDES OF SULPHURIC AND SULPHUROUS ACID.

328 When ammonia is allowed to act on a solution of sulphuryl chloride in chloroform, it yields a mixture of the amide and imide of sulphuric acid, $SO_2(NH_2)_2$ and $SO_2{:}NH$, together

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[1] See also Divers and Haga, *Journ. Chem. Soc.* 1896, 1634.

[2] Sakurai, *Journ. Chem. Soc.* 1896, 1654.

[3] Haga, *Journ. Chem. Soc.* 1904, 78.

[4] Divers, *Journ. Chem. Soc.* 1904, 108; See also Sabatier, *Compt. Rend.* 1896, **122**, 1407, 1479, 1537; **123**, 255.

[5] Trautz, *Zeit. physikal. Chem.*, 1904, **47**, 513.

with another substance which is probably aminedisulphonamide (imidosulphurylamide), $NH(SO_2NH_2)_2$.

$$SO_2Cl_2+4NH_3=2NH_4Cl+SO_2(NH_2)_2$$
$$SO_2Cl_2+3NH_3=2NH_4Cl+SO_2NH.$$

The three compounds are separated from one another and from the ammonium chloride simultaneously formed by taking advantage of the different properties of their silver salts, which after separation are converted into the free amides by the action of hydrochloric acid.

Sulphamide, $SO_2(NH_2)_2$, is best prepared by employing an excess of ammonia in the foregoing reaction, and recrystallising from ethyl acetate.[1] It is also produced, along with ammonium aminesulphonate and other compounds, when ammoniosulphonamide, $NH_4.SO_2.NH_2$, is heated at 70°, and can readily be obtained pure by means of its silver salt.[2]

It forms large colourless crystals, which are extremely soluble in water, and melt at 93°. It is converted by alkalis into salts of aminesulphonic acid (sulphamic acid) $NH_2.SO_2OH$ (p. 570), and yields a *silver* compound, $SO_2(NHAg)_2$, which is a white amorphous powder.

Sulphimide, SO_2NH, is formed together with sulphamide in the manner stated above, and is also obtained when the latter is heated above its melting point. It has not been obtained pure; its aqueous solution is fairly stable at the ordinary temperature, but on boiling is converted into ammonium hydrogen sulphate. Its *silver* compound, SO_2NAg, crystallises from hot water in long needles, which require 500—600 parts of cold water for their solution.[3]

Ammoniosulphonamide (*Ammonium amidosulphite*),

$$NH_4{\cdot}SO_2{\cdot}NH_2$$

is formed by the direct union of ammonia with sulphur dioxide and is a colourless crystalline deliquescent substance, which is converted by water into ammonium sulphite. It rapidly becomes orange coloured and decomposes at 30—35°, forming, along with other products, sulphamide and *diammoniosulphonimide* (ammonium imidosulphite), $(NH_4{\cdot}SO_2)_2NH$. This substance crystallises from alcohol in minute micaceous needles and is

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[1] Ruff, *Ber.* 1903, **26**, 2900.

[2] Divers and Ogawa, *Journ. Chem. Soc.* 1902, 504.

[3] Traube, *Ber.* 1893, **26**, 607.

soluble in water, but is slowly hydrolysed, forming ammonium aminesulphonate and thiosulphate.[1]

Nitrogen Selenide, N_2Se_2.—This compound is formed by the action of ammonia on selenium tetrachloride. It is an orange-yellow mass, which, on heating to 200°, as well as by slight pressure, detonates strongly.

THE ATMOSPHERE

329 The term *air* was used by the older chemists in the general sense in which we now employ the word *gas*, to signify the various kinds of aeriform bodies with which chemistry has made us familiar. At the present day, however, we confine the signification of the word air to the ocean of aeriform fluid or the atmosphere (ἀτμός, vapour, and σφαῖρα, a sphere) at the bottom of which we live and move.

Of the existence of an invisible gaseous envelope lying above the solid mass of the earth's crust, we become aware by the resistance offered to our bodies when we pass rapidly from place to place, as well as by the effects produced by the motion of the particles of the atmosphere which we term wind. The most convincing proof of the existence of the air is, however, given by showing that air has weight. This can readily be done by hanging a large thick-walled glass globe, closed with a cork through which a tube passes, furnished with a stopcock, on to one end of the beam of a balance, and placing weights in the opposite pan until the arrangement is in equilibrium. On exhausting the globe by placing it in communication with an air-pump, and again weighing the globe partially freed from air, the weight will be seen to be considerably less than that which it possessed before the evacuation.

A knowledge of the composition of the atmosphere forms the beginning of the present epoch of chemical science, experiment having shown, in opposition to the older views, that the air is not a simple body, but consists mainly of two different kinds of air or gases, oxygen and nitrogen.

Although some of the ancients, especially Vitruvius, appear to have held the view that the air possesses weight, yet it is to Torricelli that we owe the first distinct proof that this is the

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[1] Divers and Ogawa, *Journ. Chem. Soc.* 1901, 1099.

FIG. 144.

case. In the year 1640 a Florentine pump-maker observed that his lift-pumps would not raise water to a height greater than thirty-two feet, and consulted his great townsman, Galileo, as to the cause of this phenomenon. Galileo does not appear to have given the correct solution, as he compared the water column to an iron rod hung up by one end, which, when long enough, will at last break with its own weight. Torricelli, however, in 1643, made an experiment which gave the true explanation of the pump-maker's difficulty. Filling with mercury a glass tube three feet in length and closed at one end, but open at the other, he closed the open end with his finger and inverted the tube in a basin filled with mercury. The mercury then sank in the tube to a certain level, whilst above this level there was an empty space, which is still called the Torricellian vacuum. Above the mercury in the basin was water, and Torricelli then raised the tube so that the open end came into the water. The mercury then flowed out and the water rushed up, completely filling the tube. Fig. 144 represents the actual tubes employed by Torricelli, photographed from the original instruments placed in the Science Loan Exhibition at South Kensington. The rise of mercury or water in a vacuous tube is caused by the pressure of the atmosphere; the water is, however, 13·6 times lighter than the mercury, and hence the column of the former liquid which is supported by the atmospheric pressure is 13·6 times as high as that of the latter liquid. Thus was the *barometer* discovered, though this name was first made use of by Boyle.[1]

Hearing of Torricelli's discovery Blaise Pascal resolved to put this theory to a further test.

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[1] See *New Experiments on Cold*, published 1664-5, Boyle's *Works* (Edn. 1772), vol. ii. p. 487. "The *barometer*, if to avoid circumlocutions I may so call the whole instrument, wherein a mercurial cylinder of 29 or 30 inches is kept suspended, after the manner of the Torricellian experiment."

If, argued he, the suspension of the mercury in the barometric tube is due to the pressure or weight of the air, the mercurial column must sink when the barometer is taken to the top of a mountain, owing to the pressure on the mercury being lessened. Unable to try this experiment himself Pascal instructed his brother-in-law, Périer, to ascertain whether this was so or not, and on September 19, 1648, Périer took a barometer to the summit of the Puy-de-Dôme, and showed that the mercury sank as he ascended, proving conclusively the correctness of Torricelli's explanation.

A simple arrangement enables us to reproduce this experiment in the lecture-room; a barometer tube filled with mercury is inverted over mercury contained in a small trough, when the mercury will be seen to sink to a certain level, the space above this being vacuous. A tubulated receiver furnished with a tight-fitting caoutchouc stopper is then brought over the tube and trough, and the air pumped out from the interior of the receiver. As the pressure of the air is by degrees removed, the level of mercury in the tube will gradually become lower, until at last it will nearly, but not quite, reach the level of the mercury in the trough. On opening the stopcock the air will rush in, and the level of the mercury in the tube will rise until it has attained its former elevation.

330 Following, then, the laws of gravitation, the air forms part of the earth's body, and accompanies the solid and liquid portions in their axial and orbital motions. The absolute height to which the atmosphere extends above the earth's surface has not been ascertained with accuracy. As its density is not uniform, but diminishes as the distance from the earth's surface increases, the exact point at which the atmosphere terminates is difficult to determine. The height is certainly not uniform, inasmuch as owing to the variation of gravitation at the poles and at the equator, and owing also to the different velocities of rotation as well as to changes of temperature, a column of polar air is considerably shorter than a column of equatorial air.

The atmospheric pressure at the sea's surface would naturally be constant if it were not that owing to the variations in the solar radiation, the temperature, and, therefore, the pressure of the air, undergoes frequent alterations. These irregular variations necessitate our reading off the height of the barometer whenever volumes of gas have to be measured. There is no doubt that the atmosphere has a limit, and, from observations of the time during which the twilight extends to the zenith, it appears that the atmosphere reaches in a state of sensible density to a height of from forty to forty-five miles above the earth's surface. The relation between this height and the diameter of the earth may be illustrated by the statement that if a globe of one foot in diameter represents the earth, a film of air $\frac{1}{12}$ of an inch in thickness will represent the atmosphere.

If the air were an incompressible fluid, instead of being an elastic one, and if it had throughout the density which it possesses at the sea's level, the height of the atmosphere would be

$$10513 \times 0{\cdot}760 = 8360 \text{ meters, or } 5{\cdot}204 \text{ English miles.}$$

As, however, the air is elastic, it diminishes in density as the distance from the earth's level increases; thus at a height of 5528 metres, the air expands to twice its volume; whilst at a height of twice 5528 metres the density of the air is only $\frac{1}{3}$ of that which it possesses at the sea's level. At greater elevations the volume increases in the following ratios:—

Geographical Miles.	Volume.
0·000	1
0·587	2
1·174	4
1·761	8
2·348	16
2·935	32
3·522	64

According to the corrected determinations of Regnault, one litre of dry pure air at 0°, and under the pressure of 760 mm., at the latitude of Paris weighs 1·29349 gram, whilst according to Lasch[1] the weight at Berlin is 1·293635 gram, or almost exactly $\frac{1}{773}$ of the weight of water; Rayleigh has found the weight at Paris to be 1·29327 gram, and Leduc 1·29330. It must be remembered that since the composition of air varies within certain narrow limits, the weight of a given volume of it must also vary slightly.

The weight of the air at the level of the sea in our latitude is equal to that of a column of mercury at 0° of a height of

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[1] *Pogg. Ann. Ergänzungsbd.* **3**, 321.

760 millimetres, and this is taken as the normal barometric pressure. Hence, as 1 c.c. of mercury weighs 13·596 grams, the pressure exerted by the air on one square centimetre of surface at the sea's level will be 13·596 × 76 = 1033·3 grams (or nearly 15 lbs. on every square inch).

In common with all bodies at the earth's surface, the human frame has to support this weight, but, under ordinary circumstances, the pressure is exerted in all directions, and it is not felt. If, however, the pressure in one direction be removed, as when the hand is placed over the open end of a cylinder from which the air is being pumped out, the weight of the air is at once perceived. As the air follows Boyle's law, its density being directly proportional to the pressure to which it is subjected, it follows that when the height above the sea level increases by equal intervals, the density of the air decreases in a geometric ratio. The difference in height of two stations in the same vertical line is therefore in the ratio of the difference between the logarithms of the barometric readings at the two stations, and, if the temperature of the two stations be the same, we need only multiply the difference of the logarithms of the two readings (reduced to 0° for the expansion of mercury) by the number 18363 to obtain the elevation in metres.

The average or mean annual *temperature* of the air, like its density, is not the same throughout the mass. It diminishes as the elevation above the earth's surface increases, so that at a certain height, differing for different latitudes, a line is reached at which the mean temperature of the air does not rise above the freezing point. This is called the line of perpetual snow. At latitude 75° it reaches the sea level, in the latitude of 60° it is found at a height of 3,818 feet, whilst under the equator the snow-line exists at a height of 15,207 feet above the sea. The height of the snow-line is also affected by local causes, and is found to vary considerably even in the same latitude.

Owing to the unequal heating effect produced by the sun on different portions of the earth's surface, great variations are observed in the temperature of the atmosphere in different places, and these give rise to those motions of the atmosphere which are termed winds. Winds may either be caused by local alterations of temperature confined to narrow limits, as with the land- and sea-breezes of our coasts, or they may be produced by a general unequal diffusion of heat over the surface of the globe, as with the so-called trade-winds, which are caused by the temperature of the air in the equatorial zones being higher than that of the air in the polar regions.

331 Air was first liquefied by Cailletet,[1] and liquid air was then more closely investigated by Wroblewski[2] and Dewar, and can now be obtained in any desired quantity by the methods already described (p. 109). The composition of the liquid obtained varies with the exact method of liquefaction, owing to the difference between the boiling points of oxygen and nitrogen, and hence also the nitrogen boils off more rapidly than the oxygen. Liquid air has become a very valuable means of investigation in all researches in which low temperatures are required, and has been employed very largely for the liquefaction of other gases, for the production of high vacua, and for the study of chemical action and the properties of matter at low temperatures.

THE COMPOSITION OF THE ATMOSPHERE.

332 Atmospheric air, in addition to oxygen and nitrogen, contains as normal constituents, argon and the other gases of the helium group, aqueous vapour, carbon dioxide, ammonia, hydrogen, oxides of nitrogen and some active oxidising agent, which is perhaps ozone or hydrogen peroxide. Other gases and vapours do indeed occur in different places, under a variety of circumstances and in varying quantities. Furthermore, certain substances, such as common salt, ammonium nitrate, and some other salts, occur as finely divided solid particles, together with other minute floating material of animal, vegetable, and mineral origin.

The discovery of the composition of the atmosphere has been described in the Historical Introduction. We saw there that we owe to Cavendish the first exact determination of the relation existing between the two important constituents, oxygen and nitrogen.[3] "During the last half of the year 1781," he writes, "I tried the air of near sixty different days in order to find whether it was more phlogisticated at one time than another, but found no difference that I could be sure

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[1] *Compt. Rend.* 1877, **85**, 1270.

[2] *Monatsh.* 1885, **6**, 204; *Compt. Rend.* 1886, **102**, 1010.

[3] *Phil. Trans.* 1783, p. 106. "An Account of a New Eudiometer."

of, though the wind and weather on these days was very various, some of them being very fair and clear, others very wet, and others very foggy."[1] This result was founded on a long series of experiments, for seven or eight analyses of air collected on the same day were made by different processes, so that altogether Cavendish cannot have made fewer than 400 determinations of the composition of atmospheric air. Experiments were likewise made to see whether London air differed from that of the country, and slight differences were sometimes found in favour of London air in Marlborough Street, sometimes in favour of country air in Kensington. On taking a mean of the numbers no difference whatever was perceptible, the result of all his experiments being that 100 volumes of air contain 20·83 parts by volume of dephlogisticated air or oxygen.

The constant results thus obtained by Cavendish led several chemists, such as Prout, Döbereiner, and Thomson, to maintain that the air is a chemical compound of one volume of oxygen with four volumes of nitrogen. Against this assumption John Dalton protested,[2] insisting that the air is merely a mechanical mixture of constant composition, and contending that, because nitrogen is lighter than oxygen, the relative amounts of the two gases must vary at different heights above the earth's surface, the oxygen diminishing and the nitrogen increasing as we ascend. This view was, however, shown to be erroneous by Gay-Lussac and Thénard, who collected air in a balloon at an elevation of 7,000 metres, and found it to contain exactly the same proportional quantity of oxygen as that collected at the same time in Paris and analysed in the same way. Their results have since been corroborated by the more exact investigations of Brunner, who analysed the air collected at the top and at the bottom of the Faulhorn and found in each case exactly the same proportion between the oxygen and the nitrogen.

The very important question whether the composition of the air undergoes variation, under varying conditions of time and place, and what is the percentage of oxygen it contains was further investigated by many chemists. Gay-Lussac and Humboldt, in Paris, found that the air contained from 20·9 to 21·1 per cent. of oxygen; Davy, in London, obtained from 20·8

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[1] *Phil. Trans.* 1783, p. 126.

[2] *Manchester Memoirs*, 2nd series, vol i. 244.

to 21·1 per cent.; Thomson, in Glasgow, 21·1; and Kuppfer, in Kasan, 21·1 per cent. of oxygen. In order to obtain definite results it was, however, necessary that more accurate methods of analysis should be employed.

333 For this purpose two processes are now used, viz., (1) measurement of the volumes of the component gases, (2) determination of their weight. The first of these processes, or the eudiometric method, has been practised by Regnault, Bunsen, Lewy, and Angus Smith, whilst the latter method was chiefly used by Dumas and Boussingault in their celebrated research carried out in the year 1841.[1] In their analyses of air by the latter method, the two French chemists employed an apparatus shown in Fig. 145. The large balloon (V) was rendered as perfectly vacuous as possible, and brought in connection with the vacuous tube (*a b*), containing metallic copper reduced by means of hydrogen, and placed in a furnace in which it could be heated to redness by means of charcoal or gas. At the other end this tube was connected with the tubes C and B, and with the bulbs A; these last contained caustic potash, and the others pumice-stone moistened with strong sulphuric acid for the purpose of taking up all moisture from the air, as well as of abstracting from it the whole of its ammonia and carbon dioxide. As soon as the tube *a b* had been heated to dull redness the stopcocks *r* were opened so as to let the air pass slowly into the apparatus. Entering the tube *a b*, and coming in

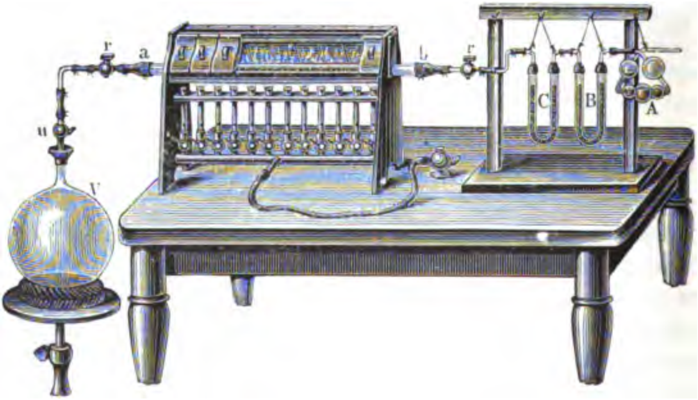

FIG. 145.

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[1] *Ann. Chim. Phys.* 1841, [3], **3**, 257.

contact with the glowing copper, the whole of the oxygen was absorbed, only the nitrogen going over into the vacuous globe. When the experiment was complete, the stopcocks were closed, the tube and balloon detached from the apparatus and each accurately weighed. Both tube and balloon were then again rendered vacuous, and weighed a third time. The tube containing the copper oxide, which had been weighed empty to begin with, was thus weighed full of nitrogen, after which the nitrogen was withdrawn by the air-pump and its weight again determined. The following details of an actual experiment may illustrate the method :—

	Grams.
Vacuous tube containing copper before the experiment	647·666
Tube filled with nitrogen and copper after the experiment	651·415
Vacuous tube after experiment	651·346
Balloon containing nitrogen at 19° and under pressure 762·7 mm.	1403·838
Balloon, vacuous, at 19°·4 and 762·7 mm. . .	1391·534

Hence, the weight of oxygen is found to be 3·680 grams, whilst the weight of nitrogen in the balloon was 12·304 grams, and the weight of nitrogen in the tube 0·069, giving a total of 12·373 grams.

Or the percentage composition is : —

Oxygen	22·92
Nitrogen	77·08
	100·00

Dumas and Boussingault used two balloons, with which they obtained the following results :—

	Percentage by weight of oxygen.	
1841.	With small balloon.	With large balloon.
April 27	22·92 . . .	22·92
„ 28	23·03 . . .	23·09
„ 29	23·03 . . .	23·04
Mean	22·993 . . .	23·016

The mean of these determinations is 23·005 parts by weight of oxygen and 76·995 of atmospheric nitrogen.

These experiments were subsequently repeated by other chemists, with the following results:—

	Mean percentage by weight of oxygen.
Lewy, in Copenhagen, 1841	22·998
Stas, in Brussels, 1842	23·100
Marignac, in Geneva, 1842	22·990

According to these experiments, therefore, the air free from carbonic acid and moisture contains about 23 parts by weight of oxygen and 77 parts by weight of nitrogen and gases of the helium group.

If the composition of air by weight be calculated from its volumetric composition by the aid of the known specific gravities of nitrogen and oxygen, the numbers obtained are:—

Oxygen	23·2
Nitrogen, &c.	76·8
	100·00

and these numbers have also been obtained experimentally by a gravimetric method by Leduc.[1]

334 This method, although capable of giving exact results, requires large apparatus and good air-pumps and balances. It can only be carried on in a laboratory, and it necessitates the employment of large volumes of air. The *eudiometric* or volumetric method is less difficult and tedious, so that the determinations may be repeated by thousands and require a much smaller volume of air. This method is liable to so small an experimental error that, with an observer well skilled in its use, it never reaches the $\frac{1}{10000}$ part, and may sometimes not exceed the $\frac{1}{100000}$ part of the whole.

The process depends on the well-known fact that when oxygen and hydrogen gases are mixed and fired by an electric spark, they unite to form water in the proportion of one volume of the former to two volumes of the latter. The volume of the liquid water formed (p. 272) is so small in proportion to that of the constituent gases that, except in cases of very exact estimations, it may be altogether neglected. Hence if we bring together a given volume of air and more hydrogen than is needed to combine with the oxygen in it, and if an

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[1] *Compt. Rend.* 1891, **113**, 129.

electric spark be passed through the mixture, one-third of the observed contraction will be due to the oxygen. In order to obtain by this method exact results[1] a very carefully calibrated eudiometer is employed, 1 metre long and about 0·025 metre wide, and the observations are conducted in a space within which the changes of temperature are as small and as gradual as possible.

The air for these determinations is collected either in small flasks of about half a litre in capacity, the necks of which have been previously elongated before the blowpipe, or in long tubes, the ends of which have been drawn out. Inside the flask or tube a small piece of fused chloride of calcium is placed for the purpose of absorbing the ammonia, and a similar piece of fused caustic potash to absorb the carbonic acid, and both substances are allowed to crystallise on the sides of the glass by the addition of a drop of water. It is quite necessary to remove the carbonic acid of the air previous to analysis. Even if the quantity present were only 0·05 per cent. of the total volume, it would produce an appreciable error in the oxygen determination, carbonic acid when exploded with an excess of hydrogen in presence of the detonating mixture of oxygen and hydrogen being decomposed into an equal volume of carbonic oxide, while an equal volume of hydrogen disappears, so that the volume of combined gas would be 0·05 per cent. too large.

In carrying out this method with exactitude the same manipulatory precautions have to be attended to which have already been described in connection with the determination of the composition of water (p. 268).

The following numbers[2] show the approximation obtained by Bunsen in two analyses of the same sample of air collected in Marburg on 9th January, 1846 :—

	Volume.	Pressure. at 0°.	Temp. C.	Vol. at 0° and 1 m. pressure.
Air employed	841·8	0·5101	0·3	428·93
After addition of hydrogen	1051·7	0·7137	0·3	749·77
After the explosion . . .	878·8	0·5460	0·3	480·09

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[1] For details on these points Bunsen's *Gasometry* may be consulted.

[2] Bunsen's *Gasometry*, 71.

Composition of Air in 100 *parts by volume.*

Nitrogen	79·030
Oxygen	20·970
	100·000

Air employed	859·3	0·5225	0·6	448·00
After addition of hydrogen	1051·9	0·7079	0·6	743·01
After the explosion	870·3	0·5317	0·6	461·72

Composition of Air in 100 *parts by volume.*

Nitrogen	79·037
Oxygen	20·963
	100·000

Bunsen, who brought all the processes of gas analysis to a marvellous degree of perfection, points out[1] that in normal determinations of the composition of the air still greater precision may be attained by repeating, several times, and at regular intervals, the observation of the height of the mercury in the eudiometer. From the agreement between the reduced volumes which are read off, the point in the series of observations is found at which the temperature has been most constant. As an example of such an accurate analysis Bunsen gives the following:—

—		Vol.	Press.	Temp.	Vol. at 0° C. and 1 meter pressure.	
Air employed	6h 0′	754·9	0·5045	15·4	360·52	360·62
	7 0	755·0	0·5046	15·4	360·63	
	8 0	755·2	0·5047	15·5	360·70	
After addition of hydrogen	11 0	904·0	0·6520	15·8	557·20	557·20
	12 0	904·6	0·6521	16·0	557·24	
	1 0	904·9	0·6518	16·0	557·17	
After the explosion	3 0	732·3	0·4781	16·1	330·64	330·54
	4 0	732·5	0·4777	16·1	330·45	
	5 0	732·7	0·4777	16·1	330·54	

Hence Nitrogen	79·036	volumes.
„ Oxygen	20·964	„
	100·000	„

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[1] *Gasometry*, 77.

As the result of twenty-eight analyses Bunsen found the average percentage of oxygen to be 20·924 volumes, whilst the lowest percentage found was 20·840.

Regnault,[1] using a different volumetric method, has analysed a very large number of samples of air collected in a uniform manner in various quarters of the globe, according to instructions which he had given. The error of two analyses made on the same sample rarely reached 0·02 per cent. In more than 100 samples of air collected in or near Paris, Regnault found a maximum amount of 20·999, a minimum of 20·913, and a mean percentage of 20·96 of oxygen. The difference of 0·086 per cent. is too large, according to Regnault, to be due to errors of experiment, and it must, therefore, be ascribed to variations in the composition of the air occurring from day to day.

Air collected from other localities gave Regnault the following results:—

				Percentage of oxygen.
9	samples	from	Lyons gave	20·918 to 20·966
30	„	„	Berlin	20·908 „ 20·998
10	„	„	Madrid	20·916 „ 20·982
23	„	„	Geneva and Chamounix . .	20·909 „ 20·993
17	„	„	Toulon Roads and Mediterranean	20·912 „ 20·982
5	„	„	Atlantic Ocean	20·918 „ 20·965
2	„	„	Ecuador	20·96
2	„	„	Summit of Pichincha . . .	20·949 „ 20·988
2	„	„	Antarctic Seas	20·86 „ 20·94

The conclusion which Regnault draws from these determinations, and which all subsequent observers have confirmed,[2] is, that the atmosphere shows perceptible, though very small, alterations in the amount of oxygen at different times and in different localities. This variation ranges from 20·9 to 21·0 per cent., but from special unknown causes the amount of oxygen seems sometimes to sink in tropical countries as low as 20·4 per cent., as was seen in the Bay of Bengal on March 8, 1849.

335 Angus Smith[3] has extended our knowledge of the

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[1] *Ann. Chim. Phys.* 1852, [3], **36**, 385.

[2] Morley, *Amer. Journ. of Science*, 1880, **22**, 429; *Chem. News*, 1882, **45**, 283; Hempel, *Ber.* 1885, **18**, 267, 1800; 1887, **20**, 1864; Leduc, *Compt. Rend.* 1894, **117**, 1072; 1898, **126**, 413.

[3] *On Air and Rain*, Longmans, 1872.

variations which the percentage of oxygen undergoes in the air of towns and that of closed inhabited spaces. He finds that the percentage of oxygen in air from the sea-shore, and from Scotch moors and mountains, is as high as 20·999. In the free air of towns, and especially during foggy weather, it may sink to 20·82. In inhabited rooms and crowded theatres the percentage of oxygen may sink sometimes to 20·28 (Lewy); whilst, according to the very numerous (339) analyses of Angus Smith,[1] the percentage of oxygen in mines does not average more than 20·26. The exact composition of the air at high elevations has been investigated by Frankland,[2] who has shown that, as far as nitrogen and oxygen are concerned, the composition of the air up to an elevation of 14,000 feet is constant, and that the variations exhibited in air collected at the above height fall within the limits noticed by former experimenters.

336 That the oxygen and nitrogen of the air are mechanically mixed and not chemically combined is seen from the following facts :—

(1) The quantities of nitrogen and oxygen in the air do not present any simple relation to the atomic weights of these elements, and, indeed, the proportions in which they are mixed are variable.

(2) On mixing oxygen and nitrogen gases mechanically in the proportion in which they occur in air, no contraction or evolution of heat is observed, and the mixture behaves in every way like air.

(3) When air is dissolved in water, the proportion between the oxygen and nitrogen in the dissolved air is quite different from that of the undissolved air, the difference being in strict accordance with the laws of gas-absorption on the assumption that the air is a mixture. When water is saturated with air at any temperature below 30°, the following is the proportion of oxygen and nitrogen contained in the dissolved and the original air :—

	Air dissolved in water.	Air undissolved in water.
Oxygen	35·1	20·96
Nitrogen	64·9	79·04
	100·0	100·00

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[1] *On Air and Rain*, p. 106.

[2] *Journ Chem. Soc.* 1861, **13**, 22.

If the air were a chemical combination of oxygen and nitrogen, such a separation by solution would be impossible.

(4) When liquefied air is allowed to boil, the nitrogen passes off much more rapidly than the oxygen, which could not take place if the two gases were chemically combined.

In order to show the composition of the air, the apparatus Fig. 146 is often used. This consists of a calibrated and divided glass tube filled to a given point with air over mercury. Into this is introduced a small piece of phosphorus supported upon a copper wire. Gradually all the oxygen is absorbed and the mercury rises in the tube. After a while the volume of residual gas is read off, and, corrections having been made for temperature and pressure, it is found that 100 volumes of the air contain about 21 volumes of oxygen.

Fig. 146.

Fig. 147.

Another less exact but more rapid method of exhibiting the same fact is carried out by help of the arrangement shown in Fig. 147. In the beaker-glass (*c*) is placed the iron stand (*d*) carrying the iron cup (*e*), containing a small piece of phosphorus. Over this stand is placed the tubulated cylinder (*a*). The upper part of this cylinder is graduated into five equal divisions, and water is poured into the beaker-glass until the level reaches the first division. The phosphorus in the cup is ignited by dropping down on it a chain which has been heated in a flame. The phosphorus then burns, the fumes of phosphorus pentoxide are absorbed by the water, and, when the gas has cooled, and the pressure been equalised by bringing the level of the water outside up to that inside the cylinder, four-fifths of the original volume of the air remain unabsorbed.

337 *Argon and other Gases of the Helium Group.*—As already mentioned, the residue left after the removal of the oxygen from dry air freed from carbon dioxide is not pure nitrogen but a mixture of this with argon and other gases. The amount of argon present appears to be about 0·937 part by volume in 100 of air, so that the residual "atmospheric" nitrogen contains 1·183 per cent. of argon by volume. The proportion of the other gases of the group is as follows:

Neon	1—2	vols. in	100,000	vols.	air.
Helium	1—2	„ „	1,000,000	„	„
Krypton . . .	1	„ „	1,000,000	„	„
Xenon	1	„ „	20,000,000	„	„

A comparatively large amount of helium is constantly being given off into the air from various mineral springs, and this gas also seems to be formed by the decomposition of radium, so that the amount present tends to increase. On the other hand, it is probable that owing to its molecular velocity it rapidly passes out of the atmosphere into space (Johnstone Stoney), and if this be so, the amount present at any moment represents the resultant of these two opposing tendencies.

Taking into consideration only the argon, the composition of normal air may be stated as follows (Leduc):—[1]

	By volume.	By weight.
Oxygen	21·00	23·2
Nitrogen	78·06	75·5
Argon	0·94	1·3
	100·00	100·0

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[1] *Compt. Rend.* 1896, **123**, 805.

OTHER SUBSTANCES PRESENT IN SMALL QUANTITY IN THE ATMOSPHERE.

The carbonic acid, aqueous vapour, organic matter, and the other constituents of the atmosphere vary in amount in different places and at different times much more than the oxygen and nitrogen.

338 *Atmospheric Carbonic Acid.*—Reference has already been made to the part played by atmospheric carbon dioxide (carbonic acid). The whole vegetable world depends for its existence on the presence of this gas, which serves, in the sunlight, as the chief food of plants.

The normal amount of carbonic acid existing in the air was formerly supposed to be 4 vols. in 10,000, but the investigations of the last 35 years have shown that the methods formerly in use gave too high results and that the amount is nearly 3 vols. in 10,000.[1] This number is the average of a large number of analyses of country air, but it appears that the amount is slightly greater in the night than in the day, probably owing to the influence of vegetation; over the sea the amount is also 3 vols. in 10,000, but no difference is observed between the day and night values.[2] In dull cloudy weather the amount is somewhat larger than in bright fine weather, and variations are also observed according to the direction of the wind, which when it has come over a large extent of land causes an increase in the quantity of carbonic acid.

In large towns where much coal is used, the amount of carbonic acid may rise as high at 6·0 and even 7·0 vols. per 10,000, and at high elevations the proportion of carbonic acid is generally, but not invariably, greater than at lower levels. In closed inhabited spaces the volume of carbonic acid proceeding from respiration and from the combustion of illuminating materials is usually much higher than in the open air,[3] and the proportion is much higher in mines than in the air above ground.

Air containing more than 7·0 vols. of carbonic acid per 10,000 is as a rule harmful for continued respiration; this is, however, probably not due to the carbonic acid itself, but to the other organic impurities which are formed along with it

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[1] For a full discussion of the results of the various investigators see Blochmann, *Annalen*, 1897, **237**, 39.

[2] Thorpe, *Journ. Chem. Soc.* 1867, 189.

[3] Roscoe, *Journ. Chem. Soc.* 1867, 189.

especially during respiration, for the deleterious properties of such air remain after the removal of the former gas.[1]

As the quantity of carbonic acid serves as the readiest and most reliable test of the healthiness or otherwise of an atmosphere, it becomes a matter of importance to ascertain its amount with accuracy. The methods in use for this purpose are (1) the gravimetric and (2) the volumetric method. In the first of these [2] the carbonic acid is absorbed from a known volume of air, freed from ammonia and aqueous vapour, drawn through weighed tubes containing caustic potash. This necessitates the passage of not less than forty litres of air drawn by means of the aspirator (v, Fig. 148), filled with water, through the tubes, in order that a sufficient weight of carbonic acid for an exact weighing may be obtained. The tubes A and B are filled with pumice-stone moistened with sulphuric acid. The air is thus dried and freed from ammonia. C and D contain moist but solid caustic potash for the absorption of the carbon dioxide. E and F are also drying-tubes, prepared like the tubes A and B, and

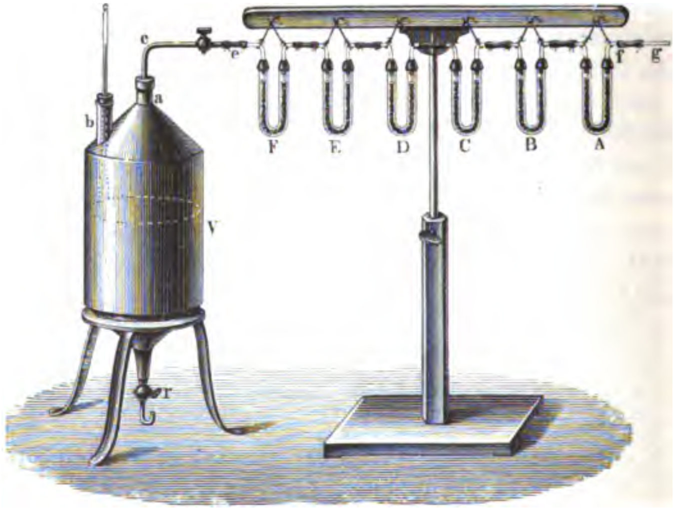

FIG. 148.

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[1] See Haldane, *Public Health*, 1904, **17**, 32; Scudder, "Report to the Home Office on Air Tests in Humid Cotton-weaving Sheds," May, 1904; "Report of Departmental Committee," March, 1897 (Roscoe, Ransome, and Roberts).

[2] Saussure, *Pogg. Ann.* 1830, **19**, 391.

serving to hold back any moisture which the dry gas might have taken up from the tubes C and D. The following example of a determination made by this plan illustrates the process :—

Gravimetric Determination of Carbonic Acid in London Air, Feb. 27, 1857.

Volume of aspirated air at 8° and under 772·5 mm. of mercury . . . . . . } = 43·2 litres.

Weight of absorbed carbonic acid . . . = 0·0308 grm.

Hence 10,000 volumes of air contain 3·7 volumes of carbonic acid.

A much more convenient process is the volumetric one proposed by Pettenkofer.[1] For this a volume of about 10 litres of air only is needed, a glass cylinder closed by a caoutchouc cap being employed, and no balance being required. The method depends upon the fact that a solution of hydrate of baryta of known strength, when shaken up with a closed volume of air containing carbonic acid, abstracts the whole of that carbonic acid from the air with formation of insoluble carbonate of barium; thus:

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

The quantity of baryta in excess which remains in solution, after shaking up with the air, is ascertained by adding to an aliquot portion of the milky fluid a standard solution of oxalic acid or sulphuric acid until the alkaline character of the baryta water disappears. When this point is reached, the whole of the residual soluble baryta has been neutralised by the oxalic acid. The baryta and oxalic acid solutions are made of such strength that equal volumes exactly neutralise each other, and so that 1 c.c. of baryta solution will precipitate exactly 1 mgrm. of carbonic acid. The following example will serve to explain this process :—

Volumetric Determination of Carbonic Acid in Manchester Air, Nov. 10, 1873.

Volume of air employed, 10·80 litres at 7° and under a pressure of 765 mm. of mercury.

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[1] *Journ. Chem. Soc.* 1858, 292.

Fifty c.c. of standard baryta solution (1 c.c. = 1 mgrm. CO_2) were shaken up with this air. Of this, after the experiment, 25 c.c. needed 22 c.c. of standard oxalic acid (1 c.c. = 1 mgrm. CO_2) for complete neutralisation. Hence 6 c.c. of baryta solution were neutralised by the carbonic acid in 10·8 litres of air; or 10,000 volumes of air contain 2·85 volumes of carbonic acid.

To obtain very accurate results by Pettenkofer's method, which is in any case more reliable than the gravimetric method, a number of precautions must be taken. For these reference may be made to Blochmann's paper.[1]

The carbonic acid may also be estimated by the direct measurement of the volume absorbed by caustic potash from a small volume of air in a modified form of gas analysis apparatus, and this method, which is very simple and rapid, appears capable of yielding very accurate results.[2]

339 *The moisture* contained in the air is liable to much more extensive changes than even the carbonic acid. Amongst the circumstances which affect the atmospheric moisture, distance from masses of water, and the configuration of the land, seem the most important. A given volume of air cannot take up more than a certain quantity of aqueous vapour at a given temperature, and then the air is said to be saturated with moisture. The weight in grams of water capable of being taken up by 1 cubic metre of air, at different temperatures, is given in the following table:—

C°.	Grams.	C°.	Grams.	C°.	Grams.
—10°	2·284	15°	12·746	35°	39·252
0°	4·871	20°	17·157	40°	50·700
5°	6·795	25°	22·843	100°	588·73
10°	9·362	30°	30·095		

This quantity is wholly dependent on the temperature of the air, being represented by the vapour pressure of water at that temperature. Thus the weight of aqueous vapour which can be taken up by 1 cubic metre of air at 10°, at which temperature its vapour pressure is 9·163 mm., is obtained as follows:— 1 cubic metre of aqueous vapour at 0° and 760 mm. weighs

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[1] *Annalen*, 1887, **237**, 39; see also Williams, *Ber.* 1897, **30**, 1450; Letts and Blake, *Proc. Chem. Soc.* 1897, 192: *Sci. Proc. Roy. Dub. Soc.* 1900, N.S. **9**, ii, 107; 1901, 436; Walker, *Journ. Chem. Soc.* 1900, 1110.

[2] Haldane, *Journ. Hygiene*, 1901, **1**, 109.

804·75 grams. Hence one cubic metre of air at 10° needs for saturation the following quantity of aqueous vapour:—

$$\frac{804{\cdot}75 \times 273 \times 9{\cdot}163}{283 \times 760} = 9{\cdot}362 \text{ grm.}$$

When the temperature of saturated air is lowered, the aqueous vapour is precipitated in the form of rain, snow, or hail, according to the temperature of the air during, or after, the deposition. If one cubic mile of air saturated with water at 35° be cooled to 0°, it will deposit upwards of 140,000 tons of water as rain, for one cubic metre of air at 35° is saturated when it contains 39·25 grams of aqueous vapour, whereas at 0° it can hold only 4·87 grams in the state of vapour. It seldom happens that the air is completely saturated with moisture, and as seldom that the amount of moisture sinks below $\frac{1}{10}$ of the saturating quantity. Even over the sea the air is never completely saturated with moisture. Large amounts of watery vapour are, however, driven by the winds into the interior of the continents, and more in summer than in winter, when the land is colder than the sea, and when, therefore, the aqueous vapour is more easily condensed, and does not so readily penetrate for great distances. The following mean pressures of aqueous vapour in the air at different places exhibit this fact clearly:—

	Mean Pressure of Aqueous Vapour in mm.		
	Mean yearly.	January.	July.
London	8·6	5·5	12·2
Utrecht	7·6	4·8	10·2
Halle	7·5	4·5	11·6
Berlin	7·3	4·3	11·1
Warsaw	6·9	3·4	11·7
St. Petersburg	5·7	2·7	10·5
Kasan	5·0	1·5	9·8
Barnaul	4·8	1·4	11·3
Urtschusk	4·0	0·4	11·3

In order to determine the amount of moisture in the air, we may employ either a chemical or a physical method. According to the first, a known volume of air is drawn through weighed tubes containing hygroscopic substances, the increase in weight of these tubes giving the weight of the aqueous vapour. Thus, 43·2 litres of London air at 8° and 772·5 mm., when passed through drying tubes, deposited 0·241 grm. of water.

In the second method *Hygrometers* are employed; of these Regnault's dew-point hygrometer is the best.[1]

340 *Ammonia* is another important constituent of the air, originating in the decomposition of nitrogenous organic matter. The relative proportion in which this substance is contained in the atmosphere is extremely small, and probably very varying, inasmuch as it is not present as free ammonia, but combined with acids, and these ammoniacal salts are washed down by the rain or absorbed by the earth. This constituent plays an important part in vegetation, for it is from it that unmanured crops derive some of the nitrogen which they require for the formation of seed and other portions of their structure.

Small quantities of nitrous and nitric acids are also found in the atmosphere, in combination with ammonia; their formation is probably due partly at any rate to the passage of electric discharges through the air, as the quantity of these compounds found in rain water falling during thunderstorms is greater than that occurring in ordinary rain. Ozone and hydrogen dioxide are also supposed to occur frequently in small quantity, but, as already stated, this cannot yet be regarded as definitely proved (pp. 264, 336).

The following observations have been made by Bechi[2] on the amount of ammonia and nitric acid contained in the rain-water falling in Florence and at Vallombrosa in the Apennines 957 metres above the sea-level for one square hectometre of surface.

	Florence.			Vallombrosa.
	1870.	1871.	1872.	
Rain in cubic metres .	9,284	10,789	12,909 .	20,278
Ammonia in grams . .	13,236	10,572	12,917 .	10,433
Nitric acid in grams. .	15,728	9,153	13,057 .	11,726

At Rothamsted in 1888–89, Warington[3] found that the total rainfall amounted to 29·27 inches, and that this contained, per million parts, 0·426 part of nitrogen as ammonia and 0·139 part of nitrogen as nitric acid, corresponding to a total weight per acre of 2·823 lbs. of nitrogen as ammonia and 0·917 lb. as nitric acid.

The amounts of these substances present in the air vary considerably in different localities.

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[1] *Ann. Chim. Phys.* 1845, [3], **15**, 129. See Scott's *Elementary Meteorology*, p. 103, (London, 1893).

[2] *Ber.* 1875, **8**, 1203.

[3] *Journ. Chem. Soc.* 1889, 537.

341 *Hydrogen, Hydrocarbons, and other Carbon Compounds.*—The existence of small quantities of hydrogen in normal air has been established by the researches of Gautier,[1] who detected it by passing very carefully dried and purified air over heated copper oxide and weighing the water produced. According to his results the amount of hydrogen present in normal air is as much as 0·02 per cent. by volume, and it is accompanied by small amounts of methane, other hydrocarbons and carbonic oxide in the neighbourhood of towns. This number, however, appears to be too high, and Rayleigh[2] has not succeeded in finding more than 0·003 per cent. of hydrogen by a similar method. Hydrogen has actually been isolated by Dewar[3] from the uncondensed residue left by the liquefaction of a large volume of air, the quantity obtained being about 0·001 per cent. of the total volume of air.

The origin of this hydrogen is to be sought in the emanations from volcanoes, the evolution of gases from granite and other igneous rocks and the products of bacterial action. As in the case of helium (p. 588), the quantity probably tends constantly to diminish owing to the escape of the gas from the atmosphere into space.

Certain oxidisable organic compounds appear to be present in air, such as formaldehyde, and a derivative, which is possibly methylal, and their amount has been estimated, by the increase which occurs in the carbon dioxide of air when it is passed over mercuric oxide at 250°, to be 2—6 grams per 100 cubic metres. An amido-derivative of formic acid seems also to be present, but in much smaller amount.[4]

342 *Atmospheric Organic Matter.*—The atmosphere also, of course, contains other gaseous bodies arising from the putrefactive decomposition of organic substances. These do not remain in the air for any length of time, but undergo fairly rapid oxidation. The particles of dust which we see dancing in the air as motes in the sunbeam are partly organic and partly inorganic. Bechi found that a thousand litres of rain water which fell in November 1870 in a garden in Florence contained 4·123 grams of total solid residue, of which one-half consisted of organic bodies and

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[1] *Ann. Chim. Phys.* 1901, [3], **22**, 5; *Compt. Rend* 1902, **135**, 1025.

[2] *Phil. Mag.* 1901, [6], **1**, 100; 1902, **3**, 416. See also Leduc, *Compt. Rend.* 1902, **135**, 860, 1332.

[3] *Proc. Roy. Soc.* 1901, **68**, 360.

[4] Levy and Henriet, *Compt. Rend.* 1898, **127**, 53; Henriet, *Compt. Rend.* 1902, **135**, 101; 1903, **136**, 1465; 1904, **138**, 1272; **139**, 67.

ammoniacal salts and one-quarter of gypsum and common salt. Amongst the organic substances the germs of plants and animals always occur, as has been proved by the classical labours of Pasteur. These bodies are the propagators of fermentation and putrefaction, and air which has been freed from these particles either by filtration through asbestos or cotton-wool, or by ignition (Pasteur), or by subsidence (Tyndall), may be left in contact for any length of time with liquids such as urine, milk, or the juice of meat, without these organic liquids undergoing the slightest change. Air which has thus been filtered is termed by Tyndall optically pure. When a ray of light is allowed to pass through air thus freed from solid particles no reflection is noticed, and the space appears perfectly empty, the motes which in ordinary air reflect the light being absent.

The organic nitrogen contained in the air, probably chiefly contained in such germinal bodies, has been quantitatively determined by Angus Smith[1] in the form of ammonia. He obtained the following results:—

	1 kilogram of air contains of organic nitrogen calculated as ammonia. Gram.
Innellan (Firth of Clyde)	0·11
London	0·12
Glasgow	0·24
Manchester	0·20
Near a midden	0·31

The volatile organic products arising from putrefaction, which are always present in the air, appear to exist in larger quantities in marshy districts than elsewhere, and in all probability they are the cause of the unhealthiness of such situations. The unpleasant odour invariably noticed on entering from the fresh air into a closed inhabited space is also due to the presence of the same organic putrescent bodies, whilst the oppressive feelings which frequently accompany a continued habitation of such spaces do not proceed from a diminished supply of oxygen, or an increase in the atmospheric carbonic acid, but are to be ascribed to the influence of these organic emanations.

343 Hence the subject of *ventilation* is one of the greatest consequence to well-being as well as to comfort, and it is necessary to provide for a continual renewal of the deteriorated air. Fortunately this renewal takes place to a considerable extent

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[1] *Air and Rain*, 438.

in a room, even when doors and windows are shut, by what may be called the natural means of ventilation, by the chimney, by cracks and crevices in doors and windows, and especially through the walls. Almost instinctively man appears to have chosen porous building materials, thus permitting by gaseous diffusion an exchange of fresh for deteriorated air. The well-known unhealthiness of new and damp houses, as well as of those built of iron, is to a great extent to be attributed to the fact that the walls do not permit a free diffusion to go on.

The fact that gases readily pass through an ordinary dry brick- or sandstone-wall, is clearly shown by the following experiment proposed by Pettenkofer. (A) Fig. 149 is a piece of wall built of ordinary brick or sandstone 82 centimetres in height, 40 cm. broad, and 13 cm. thick. On each side of the wall two rectangular plates of iron (C) are fixed, and the whole of the outside of the wall is then covered over with a coating of tar, and thus made air-tight. A tube (*c c*′) is soldered into a hole in the centre of each iron plate. If a candle-flame be held in front of the opening of the tube at one side of the wall, and a puff of air be blown from the lungs through the open end of the tube at the other side of the wall, the candle will at once be blown out; whilst if the one tube be connected by a caoutchouc tube to a gas jet, and the coal gas be allowed to pass through the tube, a flame of gas can, in a few seconds, be lighted at the open end of the opposite tube. If the bricks or stones of the experimental wall be well wetted, it will be found very difficult to blow out the candle as described.

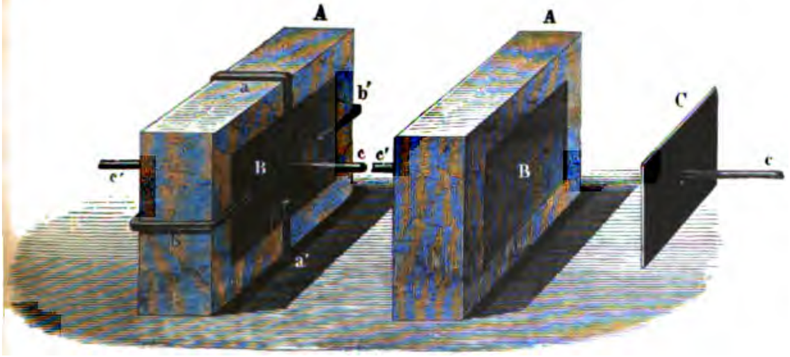

FIG. 149.

BACTERIOLOGY OF AIR.

344 The air always contains, as has been stated, a certain number of micro-organisms. These belong to the groups of moulds, yeasts, and bacteria. One litre of air contains on an average from four to five microbes. A pure unfiltered river water, on the other hand, contains from 6,000 to 20,000 in one c.c., and a fresh undisturbed soil about 100,000 microbes in one c.c.[1] The atmosphere is therefore relatively poor in micro-organisms. Their great storehouse in nature is the soil, and those present in the air are almost entirely derived from this source.

The majority of the air organisms consist of the spores of moulds and yeasts. The greater number of the bacteria found belong to the group of the micrococci, and many of these are characterised by the production of pigment when grown on culture media. *Sarcina* forms are constantly met with. The bacteria, whether bacilli or cocci, are almost entirely *saprophytic* organisms, *i.e.* organisms which are not disease-producing.[2] It is only occasionally that *pathogenic* or disease-producing forms are found, as for example the pus cocci. The spores of moulds are so light that the isolated cells can float freely in the atmosphere. The conditions are otherwise with regard to bacteria. These are not found isolated in the air, but aggregated in small groups and adhering to particles of dust. Dust is the vehicle by which they are transmitted to the air, and the bacteria therefore belong to the more ponderable elements of the air-dust. Thus, for instance, if the dust in a room be stirred up, large numbers of bacteria will be found in the air; but after the dust has once again settled to the ground, the bacteria disappear in great part, leaving the lighter free spores of the moulds in the air.

Bacteria do not pass into the air from a moist surface or from the surface of water. Indeed the air of sewers is found to contain fewer organisms than the outside air, the damp walls and the sewage retaining the organisms which are not carried about by wind. It is only when the surface containing them becomes dry that the wind is able to carry up dust and with it bacteria. The factors favouring the distribution of bacteria in the air are dryness of the soil and wind currents; the factors

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[1] Flügge, *Grundriss der Hygiene*, Leipzig, 1889.

[2] See Andrewes, *Trans. Path. Soc.* 1902, **54**, 43.

hindering their presence are moistness of the soil and a still atmosphere. The number of microbes present in the air will, accordingly, vary with the atmospheric conditions. The air contains few microbes after a prolonged fall of rain, and many after prolonged heat and dry weather. The spores of moulds, however, form an exception to this rule, as they are most abundant in the air during damp weather, moisture favouring their production. The less dust there is in the air, the less the number of bacteria, and *vice versa.* The air over the open sea and on high mountains contains few or no bacteria; the air of a town more than the air of the country. Drying being essential to the passage of microbes into the air, the forms most largely present will be those least affected by dryness, *e.g.* moulds and their spores. In the open air from 10 to 20 times as many moulds are found as bacteria. On the other hand, drying is fatal to a large number of bacteria, and especially to the pathogenic organisms, *e.g.* Koch's comma bacillus, glanders bacillus, &c. It would therefore seem that the dangers of air infection have been over-estimated. The air of enclosed spaces and dwelling-houses is richer in microbes than the open air.

It thus appears that the most dangerous factor, hygienically, is not the air itself nor the gases and sewage emanations that may be present in it, but the dust to which bacteria cling. The dust of dwellings may, therefore, become an important factor in carrying infectious microbes, more especially by fragments of clothing, linen, &c., from sick people and their attendants. Cornet found that the dust of dwellings contains the tubercle bacillus, and that such dust can produce an infection with tubercle.[1] The dust in the air of dwellings and hospitals is infectious for animals, and may produce tubercle, malignant œdema, tetanus, or septic peritonitis.

345 The great majority of air microbes are, however, saprophytic, and amongst them always occur the organisms to which fermentation and putrefaction are invariably due (Pasteur, Tyndall). A knowledge of their nature and action is important for industries in which fermentation is an essential feature, as the presence of strange forms may be injurious to the processes involved. The number of these special forms present in the air also varies according to the locality, weather, and season of the year. There are fewer in the open air than in dwellings, in

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[1] *Zeitschrift für Hygiene*, 1889, **5**, 98.

cold weather than in hot weather, and in winter than in summer. Pasteur, and later Hansen, found a relatively small number of saccharomyces (yeast-plant) in the open air. The germs of the alcoholic fermentation are however already present on the surface of fruits, &c., and do not require to be introduced from the air.[1]

The methods of examining the air for microbes fall into two groups:—

I. The methods of Miquel and their modifications. The air is filtered through glass-wool or soluble filters, and the filters are then distributed in flasks of nutrient bouillon.

II. The method in which Koch's nutrient gelatin is used directly or indirectly.[2] The air may be aspirated over nutrient gelatin in Hesse's tubes, or through soluble or insoluble filters (sugar, sand, &c.). In the latter case the filters and the microbes are distributed on gelatin culture plates. One of the best methods is that devised by Petri,[3] in which the air is aspirated through previously sterilised sand filters.

By means of the above methods a qualitative and quantitative examination of the air microbes can be carried out. For other points concerning the hygienic relations of the air Dr. Renk's book should be consulted ("Die Luft," *Handbuch d. Hygiene*, Leipzig, 1886), and also the monograph on "Air" in *A Treatise on Hygiene and Public Health*, vol. i. (London: J. & A. Churchill, 1893).

PHOSPHORUS. P = 30·77 (H = 1)
= 31·0 (O = 16)

346 A considerable amount of uncertainty surrounds the discovery of phosphorus, inasmuch as several chemists have claimed the first preparation of this body, while each has contradicted the other in a variety of ways. It seems, however, tolerably certain that phosphorus was first prepared (1674) by the alchemist Brand,

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[1] Hansen's important investigations, and the zymotechnical methods employed by him, are fully described in Jörgensen's book, *Die Mikroorganismen der Gährungsindustrie* (Berlin, 1893). The book also contains references to all the most important papers. The micro-organisms of the air have been specially studied by Miquel, and a full account of his results is contained in the issues of the *Annuaires de Montsouris* (1879, 1884, 1886, &c.).

[2] Welz, *Zeitschrift für Hygiene*, 1891, **11**, 121; Uffelman, *Archiv für Hygiene*, 1888, **8**, 262.

[3] *Zeitschrift für Hygiene*, 1888, **3**, 1.

of Hamburg, who obtained it from urine in a process which had been previously made use of for the purpose of preparing a liquid supposed to have the power of turning silver into gold. By a secret process, Brand succeeded in preparing phosphorus from this liquid, and he is said to have sold the secret of the manufacture to Krafft, from whom it appears that Kunkel learnt what he knew, and published in the year 1678 a pamphlet on this remarkable product.[1]

In those early days phosphorus was a very costly body, being valued as one of the most remarkable and interesting of chemical substances. Krafft exhibited it as one of the wonders of nature to various crowned heads, amongst others, in the year 1677, to King Charles II. of England. Robert Boyle became acquainted with its existence without, as he tells us, having been informed by Krafft of the mode of preparation, except so far as that it was obtained from an animal source, and he succeeded in the year 1680 in the preparation of phosphorus, as Kunkel and Brand had done before him, by strongly heating a mixture of evaporated syrupy urine and white sand in an earthenware retort.[2] The difficulty of thus preparing phosphorus was considerable, and so many chemists failed in the attempt that the price, as late as the year 1730, was extremely high, ranging from ten to sixteen ducats the ounce. Gahn, in 1769, discovered the existence of calcium phosphate in bones, but it was not until this fact was published by Scheele in 1771 that phosphorus was obtained from bone-ash, which has from that time invariably served for its preparation.

The name phosphorus (φῶς, light, and, φέρω, I bear) was originally used to designate any substance which was capable of becoming luminous in the dark. The first chemical substance in which this property was noticed was termed *Bonnonian phosphorus* (see barium sulphide). In order to distinguish true phosphorus from this body, the name of *phosphorus mirabilis*, or *phosphorus igneus*, was given to it. In the eighteenth century it was usually termed Brand's, Kunkel's, or Boyle's phosphorus, or sometimes English phosphorus, because it was then prepared in London by Hankwitz in quantity according to Boyle's receipt.

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[1] "Oeffentliche Zuschrift vom Phosphor Mirabile und dessen leuchtenden Wunderpilulen."

[2] Boyle, *Phil. Trans.*, 1693—"A Paper of the Hon. Robert Boyle, deposited with the Secretary of the Royal Society on the 14th of October, 1680, and opened since his death."

Up to the time of Lavoisier, phosphorus was considered to be a compound of phlogiston with a peculiar acid; but in 1772 the great French chemist showed that the acid body formed by the combustion of phosphorus weighed more than the phosphorus itself, the augmentation in weight being due to a combination with a constituent of the air.[1] In a memoir communicated to the Academy in 1780, he represented phosphoric acid as a compound of phosphorus and oxygen, and investigated its salts.

347 Phosphorus, being a very easily oxidisable body, does not, of course, exist in the free state in nature. It is, however, very widely distributed, especially in combination with oxygen and calcium as calcium phosphate. The most important minerals containing phosphorus are estramadurite or phosphorite, $Ca_3(PO_4)_2$; sombrerite, an impure calcium phosphate; apatite, $3Ca_3(PO_4)_2 + CaCl_2$; wavellite, $4Al(PO_4) + 2Al(OH)_3 + 9H_2O$; vivianite, $Fe_3(PO_4)_2 + 8H_2O$. Calcium phosphate also forms the chief constituent of coprolites, and occurs in small quantity throughout the granitic and volcanic rocks, whence it passes into the sedimentary strata, and thus finds its way into the soil.

The original observation of Gahn, that phosphorus forms an essential constituent of the animal body, might, it may be thought, have led to the conclusion that this element is very widely distributed. It was, however, reserved for a later time to show that almost all substances found on the earth's crust contain phosphorus, that it is always present in sea-water, and in all river- as well as in almost every spring-water. All fruitful soils contain phosphorus, and no plants will grow on a soil destitute of it, as it is required to build up certain essential parts of the vegetable structure, especially the fruit and seeds. From the plant the phosphorus passes into the animal body, where it is found in the juices of the tissues, but especially in the bones of vertebrate animals, the ashes of which consist almost entirely of calcium phosphate. Phosphorus is likewise always present in the nuclei of the animal cell, and when the animal tissues, whether muscular or nervous, are worn out, they are replaced by fresh material, the phosphorus in them being excreted in the urine chiefly as sodium ammonium phosphate or microcosmic salt, $Na(NH_4)HPO_4 + 4H_2O$. Phosphorus is likewise found in small quantity in meteoric stones, a fact which indicates its wide cosmical distribution.

348 *Preparation.*—The preparation of phosphorus from bones

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[1] *Opuscules Physiques et Chimiques*, 1774.

was first described by Scheele in 1775. He warmed bone-ash for many days with dilute nitric acid, precipitated the lime with sulphuric acid, evaporated the liquid from which the gypsum had separated out to a thick syrup, and distilled the residue with charcoal.[1] This process was afterwards simplified by Nicolas and Pelletier,[2] inasmuch as they treated the bone-ash at once with sulphuric acid. The yield of phosphorus by this process was, however, but small, until Fourcroy and Vauquelin[3] determined the exact proportion of sulphuric acid required for the complete decomposition of the bone-ash, thus preparing the way for the economical production of the element.

In order to obtain calcium phosphate from bones, these were formerly burnt in ovens. At present, however, the organic material contained in them is made use of in several ways. Thus, the bones are either boiled with water, or treated with superheated steam, to extract the gelatine which they yield, or they are distilled in iron retorts to obtain the ammonia and other volatile matters which they evolve. In the latter case bone-black or animal charcoal, which consists of a mixture of charcoal and calcium phosphate, is left behind. This bone-black is largely used by sugar refiners for clarifying the syrup, and it is only when it has become useless for this purpose that it is completely burnt in an open fire, and obtained in the form of bone-ash. To prepare phosphorus from bone-ash it is treated with sufficient dilute sulphuric acid to convert the whole of the calcium present into sulphate,[4] which remains as an insoluble precipitate, whilst the liberated phosphoric acid dissolves in the water. The sulphate is separated by filtering through large filter beds, washed with water till nearly free from phosphoric acid, and the filtrate concentrated to a syrup. The liquor is then mixed with about a quarter of its weight of coke or charcoal, and carefully dried in cast-iron pots or a muffle furnace, the orthophosphoric acid, H_3PO_4, being thus converted into metaphosphoric acid, HPO_3. The dried mixture is then heated to bright redness in earthenware retorts of the shape shown in Fig. 150, when the following reaction takes place :—

$$4HPO_3 + 12C = 2H_2 + 12CO + 4P.$$

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[1] *Gazette Salutaire de Bouillon*, 1775.

[2] *Journ. Phys.* 1778, **11**, 28.

[3] *Journ. Pharm.* **1**, 9.

[4] Readman, *J. Soc. Chem. Ind.* 1890, **9**, 163, 473.

The mixture of phosphorus vapour, hydrogen and carbonic oxide passes through the bent earthenware pipe (*a*), which dips under the surface of water contained in the vessel (*b*), whereby the phosphorus vapour is condensed.

A large proportion of the phosphorus made in England is prepared from sombrerite, an impure calcium phosphate found on the island of Sombrero in the West Indies. It appears that the greater part of the phosphorus made in the world is manufactured in two works—namely, that of Messrs. Albright and Wilson, at Oldbury, near Birmingham—and that of MM. Cognet et Fils, in Lyons.[1] The manufacture of phosphorus is somewhat dangerous, on account of the easy inflammability of the product, and it is also difficult, inasmuch as the distillation requires forty-eight hours for its completion,

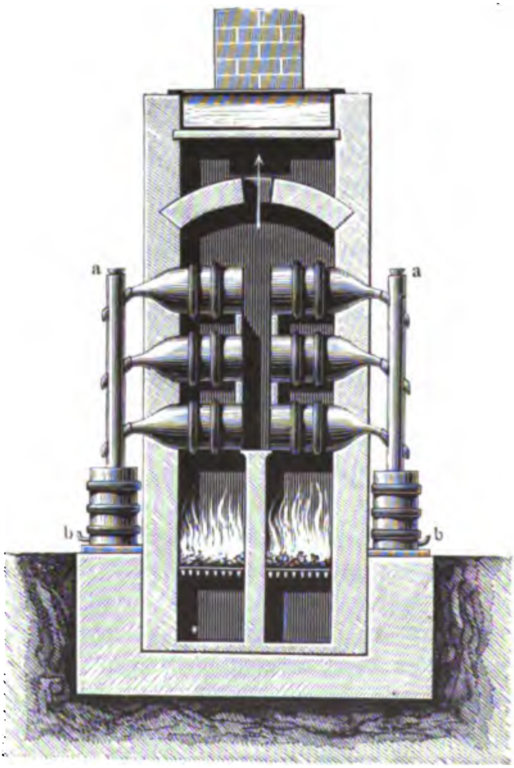

Fig. 150.

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[1] Hofmann, *Report on the Vienna Exhibition.*

and necessitates constant watching during the whole of this time.

Many other processes have been proposed for obtaining phosphorus, but, as a rule, these have not been very successful. An electrical process, however, known as the Readman, Parker and Robinson system, has been successfully carried out on the large scale, in which the phosphate is directly converted into phosphorus without previous treatment with sulphuric acid. In this process, the phosphate is mixed with charcoal and suitable fluxes, and, after being heated to as high a temperature as possible, is introduced into an electrical furnace, consisting of an iron tank lined with refractory material, and containing large carbon electrodes in the sides. Through the latter a powerful electrical current is passed, and at the high temperature thus attained phosphorus vapour mixed with other gases distils over, and is condensed in the usual manner; the residue forms a liquid slag which may be drawn off at intervals, and fresh raw material introduced into the furnace, thus rendering the process continuous.[1]

The crude phosphorus always contains small particles of carbon mechanically carried over. To get rid of this and other impurities, the phosphorus is either melted under water, and pressed through chamois leather, or, more frequently, the crude melted material is mixed with sulphuric acid and potassium bichromate, three and a half parts of each being used for every 100 parts of phosphorus. This oxidising mixture acts upon the impurities, which rise as a scum to the surface of the liquid, whilst the pure phosphorus remains clear and colourless at the bottom. It was formerly cast into sticks by the workmen sucking the melted phosphorus up with the mouth into glass tubes. Instead of this dangerous operation an apparatus is now employed by which the phosphorus is cast in brass or copper tubes by a continuous process, proposed by Seubert.[2] The apparatus consists of a copper vessel, in which the phosphorus is melted under water; from this the molten phosphorus is allowed to flow into a tube consisting of glass or copper. One half of this tube is surrounded by hot and the other by cold water, the phosphorus being removed in the form of solid sticks, and cut under water into pieces of a convenient length.

The quantity of phosphorus manufactured in the year 1874

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[1] Patents No. 14962 and 17719 (1888); *Thorpe's Dict.* **3**, 183—194.

[2] *Annalen*, 1844, **49**, 346.

amounted to 250 tons, and is at the present time (1904) probably not less than 1,200 tons, the greater portion of which is used directly or indirectly for the manufacture of lucifer matches, a certain amount being employed as a vermin poison, and a small quantity being used in chemical laboratories.

The distillation of phosphorus can easily be shown in the lecture-room, by placing some pieces of dry phosphorus in a small tubulated retort attached to a tubulated receiver containing water, which communicates with the air by means of a tube one metre in length dipping under mercury. A current of carbon dioxide gas is passed through the tubulus of the retort so as to drive out the air. As soon as all the air has been removed the phosphorus can be heated and is seen to boil, the colourless vapour condensing in transparent yellow drops on the neck of the retort and in the receiver. The barometer-tube prevents the entrance of atmospheric oxygen.

349 *Properties.*—Like sulphur and other elements, phosphorus exists in different allotropic modifications. *Common* or *octahedral phosphorus* is, when freshly prepared and kept in the dark, a slightly yellow or almost colourless body, which, when slowly solidified, is perfectly transparent, but when quickly cooled is translucent and of a wax-like character. At low temperatures phosphorus is brittle, but at 15° it becomes soft like wax, so that it may be easily cut with a knife. The mass of the substance has, however, a crystalline structure. This may be seen by leaving the solid for some time in contact with dilute nitric acid, when the surface becomes distinctly crystalline. According to v. Schrötter its specific gravity at 10° is 1·83, and it melts at 44°·3, forming a colourless or slightly yellow strongly refractive liquid, having a specific gravity of 1·764. Melted phosphorus, under certain circumstances, remains liquid for a long time at temperatures much below its melting point. This is especially the case when it is allowed to cool slowly under a layer of an alkaline liquid, or when the solution in carbon bisulphide is slowly evaporated under water. Neither solid nor melted phosphorus conducts electricity (Faraday). When heated in an atmosphere free from oxygen to a temperature of 290°, phosphorus boils, yielding a colourless vapour which, according to the experiments of Mitscherlich, has a specific gravity of 4·58 at 515°, and of 4·50 at 1040° according to those of Deville and Troost (air = 1·0). Hence the molecular weight of phosphorus between these temperatures is 123·84, or the molecule consists of four atoms.

At a temperature of 1500—1700° the vapour-density decreases, the numbers obtained falling between the values required for the formulæ P_4 and P_2, so that at this temperature the molecules P_4 are partially dissociated into lighter molecules.[1] The determination of the molecular weight of phosphorus in solution has led to different results with different investigators; thus Beckmann[2] from the boiling point of solutions of phosphorus in carbon bisulphide deduced the molecular formula P_4, which was also obtained by Hertz[3] from the freezing point of its benzene solutions. On the other hand, Paterno and Nasini[4] obtained by the latter method numbers which point to the existence of molecules P_4 and P_2 in the solution.

Phosphorus also evaporates at temperatures below its boiling point. If a small piece of phosphorus be placed in the Torricellian vacuum, it gradually sublimes, and is deposited again in the form of bright colourless crystals. Large crystals of phosphorus are obtained by placing phosphorus in a flask filled with carbon dioxide, then hermetically sealing it and allowing the bottom of the flask to be heated on a water-bath for some days to 40°; or in another way by keeping phosphorus in vacuous tubes in the dark for some time, when it sublimes and crystallises on the side of the tube in colourless, transparent, brightly shining crystals.[5]

Phosphorus is nearly insoluble in water and slightly soluble in ether, oil of turpentine, and the essential oils. It is readily soluble in chloride of sulphur, phosphorus trichloride, sulphide of phosphorus, and carbon bisulphide, of which one part by weight will dissolve from seventeen to eighteen parts of phosphorus. From solution in carbon bisulphide, phosphorus can easily be obtained in the crystalline state, usually in the form of rhombic dodecahedra. The same crystals are obtained, according to Mitscherlich, by heating under water a mixture of one part of sulphur with two parts of phosphorus. In order to obtain phosphorus in the state of fine powder, the melted substance is well shaken with cold water containing a little urea, the small drops thus formed congealing into solid particles.

Phosphorus is an extremely inflammable substance, igniting

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[1] Biltz and V. Meyer, *Ber.* 1889, **22**, 726; V. Meyer and Mensching, *Annalen*, 1887, **240**, 317.

[2] *Zeit. physikal. Chem.* 1890, **5**, 76.

[3] *Zeit. physikal. Chem.* 1890, **6**, 358.

[4] *Ber.* 1888, **21**, 2155.

[5] Herman and Maskelyne, *J. Soc. Chem. Ind.*, 1888, 9.

at 45° in the air, and is always kept under water. In presence of air and light it becomes covered under water with a white crust, which gradually falls off, whilst the phosphorus becomes darker coloured. The crust is common phosphorus, which falls off from an unequal oxidation of the mass, and on melting it under water it assumes the ordinary appearance of the element.

Phosphorus appears luminous in the dark, when in contact with moist air, and it evolves fumes possessing a strong garlic-like smell. These fumes are poisonous, producing phosphorus-necrosis, a disease in which the bones of the jaw are destroyed, and one by which scrofulous subjects are the most easily affected. The luminosity of phosphorus in the air depends upon its slow oxidation, with formation of phosphorous acid. In this act of combination so much heat is evolved, that if a large piece of phosphorus be allowed to lie exposed to the air it at last melts and then takes fire. The luminosity and oxidation of phosphorus are best seen by pouring a few drops of the solution of this body in carbon bisulphide on to a piece of filter paper and allowing the solution to evaporate. In the dark the paper soon begins to exhibit a bright phosphorescence, and after a short time the phosphorus takes fire and burns. It was formerly believed that phosphorus becomes luminous in gases upon which it can exert no chemical action, such as hydrogen or nitrogen. This is, however, not so, the luminosity which has been observed in these cases being due to the presence of traces of oxygen. From these facts it would naturally be inferred that phosphorus must be more luminous in pure oxygen than in air. Singularly enough, this is not the case.[1] At temperatures below 20° phosphorus is not luminous in pure moist oxygen, indeed it may be preserved for many weeks in this gas without undergoing the slightest oxidation.[2] If, however, the gas be diluted by admixture with another indifferent gas, or if it be rarified, the phosphorescence is at once observed (Graham). The phenomenon can be very beautifully shown by placing a stick of phosphorus in a long tube (*a*, Fig. 151), closed at one end and open at the other, and partly filled with mercury, into which some pure oxygen is brought. The open end of the tube is connected by a caoutchouc tube with the vessel (*b*) containing mercury, so that, by raising or lower-

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[1] *Quart. Journ. Science*, 1829, ii. 83.

[2] W. Müller, *Ber.* 1870, **3**, 84.

ing the vessel, the pressure on the gas can be regulated. If the pressure be so arranged that it does not amount to more than one-fifth of an atmosphere, the phosphorus will be seen to be brightly luminous in the dark. If the pressure be then gradually increased, the light will become less and less distinct, until, when the level of the mercury is the same in both vessels, the luminosity has entirely ceased. The phosphorescence can, however, at once be brought back again by lessening the pressure. The luminosity of phosphorus is also stopped when certain gases, such as sulphuretted hydrogen,

FIG. 151.

ethylene, or the vapours of certain compounds, such as ether or turpentine, are present even in minute quantities.

The water in which phosphorus has been kept is also luminous in the dark, as phosphorus is soluble, though only very slightly so, in water, 1 part dissolving in about 300,000 of water.

The rate of oxidation of phosphorus by oxygen depends very largely on the amount of water vapour present, the most rapid reaction occurring when the gas has been carefully dried over sulphuric acid. Under these circumstances oxidation commences at once at the atmospheric temperature, even when the pressure of the oxygen is as high as 1900 mm. Slow oxidation then proceeds until the pressure is about 500 mm., at which point a rapid acceleration occurs and continues until all the oxygen is absorbed, the final product being phosphoric oxide. When the vapour pressure of water in the gas amounts to 16—20 mm. no oxidation occurs until the pressure of the oxygen falls to about 500 mm. The rate of oxidation is then much less than with dried oxygen, and this appears to be due to the formation of a protective film on the phosphorus in the presence of water vapour. Both ozone and hydrogen peroxide appear to be formed in presence of excess of water, and traces of ammonium nitrate and nitrite in presence of air.[1]

When phosphorus is heated slightly above its melting-point in moist air or oxygen it takes fire and burns with a brightly luminous flame and with evolution of dense white fumes of phosphorus pentoxide, P_2O_5. The greatest precautions are necessary in working with phosphorus on account of its highly inflammable character. It must always be cut, as well as kept under water, and must not be rubbed either in contact with the skin, or when it is being dried with blotting paper, as burning phosphorus produces deep wounds, which heal only with great difficulty. Phosphorus does not, however, combine with oxygen in absence of moisture, and may be distilled in the perfectly dry gas without undergoing any change.[2]

Phosphorus combines directly with the elements of the chlorine and sulphur groups of elements, but not directly with hydrogen. If it is heated with aqueous vapour to a temperature of 250°,

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[1] Russell, *Journ. Chem. Soc.* 1903, 1263; See also Ewan, *Phil. Mag.* 1894, [5], **38**, 505; van t'Hoff, *Zeit. physikal. Chem.* 1895, **16**, 411; Centnerszwer, *Zeit. physikal. Chem.* 1898, **26**, 1; Elster and Geitel, *Phys. Zeit.* 1903, **16**, 457; Schmidt, *Ann. Phys.* 1902, **10**, 704; Schenck, *Sitzber. kgl. pr. Akad. Wiss. Berlin*, 1904, 37.

[2] H. B. Baker, *Journ. Chem. Soc.* 1885, 349; *Phil. Trans.* 1888, 582.

the water is decomposed with formation of phosphorous acid and phosphine. It also combines with most of the metals at a high temperature, and on account of its easy oxidisibility, it acts as a powerful reducing agent, precipitating certain metals, such as gold, silver, and copper, when it is brought into solutions of their salts.

350 *Detection of Phosphorus.*—The above reaction may be made use of for the purpose of detecting free phosphorus. Thus, if the material under examination be boiled with water, and the escaping vapour allowed to come in contact with a piece of paper which has been wetted with a solution of nitrate of silver, any phosphorus present will cause a black stain of metallic silver to appear on the paper. No reduction, however, takes place of a lead salt under similar circumstances, whilst if the black stain be due to the presence of sulphuretted hydrogen, the lead as well as the silver paper will become stained.

When phosphorus is boiled with water, it is partially volatilised, issuing in the state of vapour together with the steam. This property of phosphorus may be made use of for its detection in cases of phosphorus poisoning. The apparatus which is used for this purpose is shown in Fig. 152. The contents of the stomach supposed to contain the poison are diluted with water and placed in the flask A. This flask is connected by the tube *b*, with a condensing tube *c c c*, surrounded by cold water. As soon as the liquid contained in the flask is heated to boiling, some of the phosphorus, if present, is volatilised together with the steam, and if the whole of the apparatus be placed in the dark, a distinct luminosity, usually in the form of a ring, is observed at the point where the steam is condensed. If the quantity of phosphorus is not too small, some of it is found in the receiver in the form of small solid globules (Mitscherlich). This test is rendered more delicate by the occasional admission of air to the flask during the distillation.

351 *Action of Phosphorus as a Poison.*—Ordinary phosphorus is a powerfully poisonous substance capable of inducing death in a few hours, or, when given in small doses, of producing a remarkable train of poisonous symptoms lasting for many days, or even for weeks. Red phosphorus appears, on the other hand, to be without action on the animal economy, when introduced into the stomach. Although cases occur in which the administration of phosphorus is followed by death in

a few hours, more commonly some days elapse between the date of administration and death. In the more common cases of phosphorus poisoning, some time after the poison has been taken there supervenes pain in the stomach, with vomiting of garlic-smelling substances, and not unfrequently diarrhœa; all these symptoms of gastro-intestinal irritation may be, and often are, absent. Whether they are present or absent the patient soon becomes very weak, a febrile condition ensues, and the skin assumes a jaundiced hue. Hæmorrhages may occur, and, towards the end, convulsions or coma usually make their appearance.

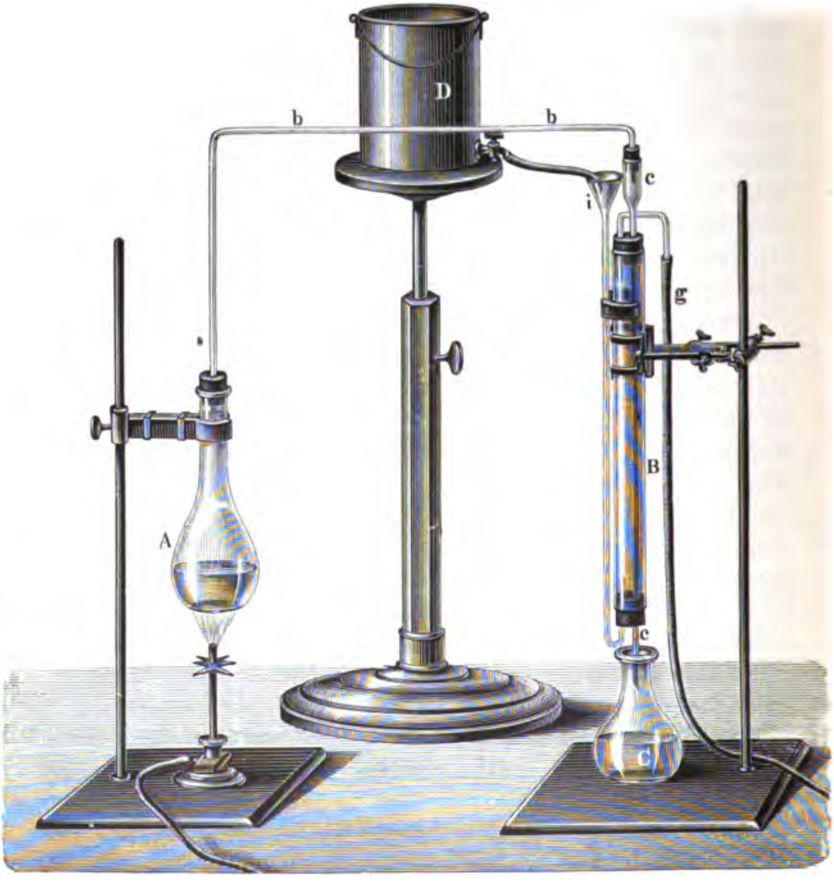

FIG. 152.

The appearances observed in the bodies of animals and men poisoned with phosphorus are very interesting and indicate that this substance produces a powerful effect upon the nutrition of the body. Minute extravasations of blood are frequently seen in the lining membrane of the stomach and intestines, and not unfrequently small ulcers occur in those organs. The common and remarkable appearances are fatty degeneration of the liver, kidneys, heart and voluntary muscles. It is to be remarked that the same changes are observed, although in a less marked degree, after chronic poisoning by arsenic, antimony, and vanadium. These fatty degenerations probably indicate that phosphorus and the allied poisons exert an influence whereby the oxidation changes, which have their seat in the animal tissues, are more or less slowed or arrested. (Gamgee).

Death has in man followed the administration of doses of phosphorus not exceeding a decigram.

352 *Red Phosphorus.*—This peculiar modification of phosphorus, formerly termed amorphous phosphorus, was discovered by v. Schrötter in 1845.[1] Other chemists had indeed previously noticed the existence of this substance, but its nature had been misunderstood. It is obtained by the action of light and heat on ordinary phosphorus. This change occurs with tolerable rapidity when the yellow phosphorus is heated from 240° to 250°. At a higher temperature red phosphorus begins to undergo the opposite change, yellow phosphorus being formed. Hence the passage from one allotropic modification to another is more readily shown in the case of phosphorus than in that of any other element. For this purpose all that is needed is a glass tube containing three bulbs (Fig. 153), and having the open end bent at right angles and dipping under mercury. In the last of these three bulbs is placed a piece of phosphorus. The phosphorus is then heated, the whole of the oxygen contained in the apparatus being very soon absorbed, and the remainder of the phosphorus is distilled from the last into the middle bulb. By gently heating this, it is transformed into the red modification, which by a further application of heat, is reconverted into the ordinary modification, which distils into the third bulb. This experiment should be made on a leaden table or on a surface covered with a coating of sand, in case the bulbs should burst.

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[1] *Pogg. Ann.* 1850, **81**, 276.

Red phosphorus is also formed when ordinary phosphorus is heated in closed vessels to 300°, or about 10° above the boiling point. In this case the change takes place in a few minutes. The conversion of ordinary into red phosphorus can also be brought about by certain chemical actions. E. Kopp[1] found, in 1844, that by the action of iodine on phosphorus a red body is formed, which on heating yields the ordinary modification of phosphorus, and B. C. Brodie[2] has shown that only a trace of iodine is needed to bring about the change from the yellow to the red modification, and that when common phosphorus is heated with a trace of iodine to 200°, a very violent reaction takes place and the red modification is formed. It is also formed by submitting ordinary phosphorus at 100° to the action of the silent discharge.[3]

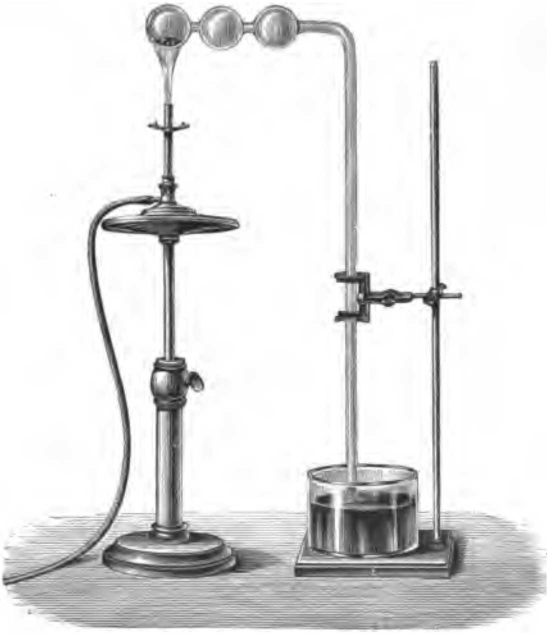

Fig. 153.

Red phosphorus is usually obtained as a compact solid substance, which has a dark reddish brown colour, and generally possesses a metallic iron-grey lustre. It has a specific gravity of

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[1] *Compt. Rend.* 1844, **18**, 871.

[2] *Journ. Chem. Soc.* 1853, 289.

[3] Burgess and Chapman, *Journ. Chem. Soc.* 1901, 1243.

2·106, exhibits a conchoidal fracture, and yields a reddish brown coloured powder closely resembling finely divided oxide of iron; its hardness lies between those of calcspar and fluorspar. It was formerly supposed to be amorphous, but Pedler[1] and Retgers[2] have shown that it is at any rate partially crystalline. According to Muthmann[3] red phosphorus is a mixture of an orange red amorphous powder with small crystals having a violet tint. It is a tasteless, odourless substance, insoluble in all those solvents which dissolve common phosphorus, and when introduced into the system in the ordinary manner is not poisonous, the whole being excreted unchanged; if, however, it is injected into the blood the usual symptoms of phosphorus poisoning occur.[4]

Red phosphorus readily dissolves in alcoholic potash, forming a deep red solution in which acids produce a red precipitate. According to Burgess and Chapman this phenomenon is simply one of solution and reprecipitation, whilst Michaelis regards it as a chemical reaction, the substance precipitated by acids being, in his view, the suboxide P_4O (p. 634).

It is usually stated that red phosphorus, when perfectly free from the ordinary modification, is unalterable in the air, but Pedler[5] has shown that at any rate in hot moist climates, this is not the case, but that it slowly undergoes oxidation, with formation of phosphorous and phosphoric acids. When heated by itself in absence of air, it does not undergo any alteration until a temperature of 350° is reached, when it is slowly converted into ordinary phosphorus, the change taking place more quickly at a higher temperature. When heated in the air it takes fire at about 260°. Ordinary phosphorus takes fire spontaneously when brought into chlorine gas, but the red phosphorus requires heating before ignition takes place. Similar differences between the two modifications present themselves in a large number of other chemical reactions, and the red modification conducts electricity, although but feebly, whilst the yellow is practically a non-conductor.

The mode of manufacturing red phosphorus is simple. Ordinary phosphorus is placed in an iron vessel and heated to a temperature of 240°. This vessel is closed by means of a cover

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[1] *Journ. Chem. Soc.* 1890, 599.

[2] *Zeit. anorg. Chem.* 1893, **3**, 399.

[3] *Zeit. anorg. Chem.* 1893, **4**, 303.

[4] Neumann, *Ber.* 1888, **21**, 748c.

[5] *Journ. Chem. Soc.* 1890, 599.

through which passes a long narrow pipe open at both ends, so that the air has limited access to the phosphorus contained in the vessel. Thus all danger of explosion is avoided, and the air in the narrow tube undergoing but little change, only a little of the phosphorus takes fire as soon as the oxygen has been withdrawn from it by the combustion of the first portion of the phosphorus. The red phosphorus thus prepared is ground under water and freed from common phosphorus by boiling with a solution of caustic soda, washing and drying. The commercial red phosphorus, when in large compact masses, almost always contains a small quantity of enclosed yellow phosphorus, and not unfrequently takes fire when it is rubbed or broken. In consequence it is usually packed in vessels containing water, whilst the ground substance, as above described, may be sent in the dry state in tin boxes. It frequently also contains traces of graphite, originating from the cast iron pots in which it is heated.

When phosphorus is heated in sealed tubes in contact with metallic lead for ten hours at a temperature approaching a red heat, and the mass then cooled, the lead is found to be permeated with small crystals, which have been formed by the phosphorus dissolving in the melted lead at a high temperature and crystallising out on cooling.[1] In order to separate these crystals from the metallic lead the mass is placed in dilute nitric acid, when the lead is dissolved. The crystals of phosphorus are still further purified by subsequent boiling in strong hydrochloric acid. The phosphorus is thus obtained as a brightly lustrous dark crystalline mass, which in thin plates possesses a red colour and consists of microscopic rhombohedra. This variety is also formed when red phosphorus is heated under pressure to a temperature of 580° (Troost and Hautefeuille).

Recent investigations show that this crystalline form of phosphorus, which is sometimes known as metallic or rhombohedral phosphorus, possesses all the properties of red phosphorus, from which it differs only in the size and development of the crystals (Pedler, Retgers, Chapman [2]).

353 *Scarlet Phosphorus.*—When a solution of ordinary phosphorus in phosphorus tribromide is boiled, a bright red variety of phosphorus gradually separates out, which is known as

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[1] Hittorf, *Pogg. Ann.* 1865, **126**, 193.

[2] *Journ. Chem. Soc.* 1899, 735.

scarlet phosphorus. It is in an extremely fine state of division and has not yet been obtained free from the solvent in presence of which it is produced. It resembles red phosphorus in many of its properties, but appears to be amorphous and is chemically very active. Thus it precipitates copper from solutions of copper sulphate, dissolves readily in alkalis, and is violently oxidised by nitric acid. It does not fume in the air and is non-poisonous. Ammonia and bases convert it into black substances which are derivatives of solid hydrogen phosphide (p. 626). When heated it becomes darker and then black, but regains its original colour on cooling. It can be used together with potassium chlorate instead of ordinary phosphorus for the production of matches which are non-explosive and may be struck on any ordinary surface.[1]

According to Thénard a fourth modification of phosphorus exists. This substance has a black colour, and is obtained when melted phosphorus is quickly cooled. It has, however, been shown that this black phosphorus is only formed when foreign bodies, especially mercury or other metals, are present, these bodies uniting with phosphorus to form a black metallic phosphide. A further modification has been described by Vernon,[2] but its existence is as yet doubtful.

354 When hydrogen is passed over phosphorus or when phosphates, hypophosphites, or phosphites, or the corresponding acids, are brought into a vessel in which hydrogen is being evolved, the hydrogen is seen to burn with an emerald green flame; and if the quantity of phosphorus be not too small, a white porcelain plate held in the flame is stained with a red deposit.[3] This reaction does not occur in the presence of alcohol, ether, or animal matter.[4] The spectrum of the phosphorised hydrogen flame exhibits three bright green lines, of which one is almost coincident with one of the lines of the barium spectrum, the third being not quite so bright, and lying between the two bright ones and the sodium line.[5]

Phosphorus is frequently used in the laboratory. It is largely employed in the manufacture of the iodides and bromides of methyl and ethyl, bodies much used in the preparation of

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[1] Schenck, *Ber.* 1902, **35**, 351; 1903, **36**, 979, 4202; Schenck and Marquart, *J. Chem. Soc. Ind.* 1903, **22**, 1226.

[2] *Proc. Chem. Soc.* 1891, 3.

[3] Dusart, *Compt. Rend.* 1856, **43**, 1126.

[4] Blondlot, *Compt. Rend.* 1861, **52**, 1197.

[5] Christofle and Beilstein, *Ann. Chim. Phys.* 1864, [4], **3**, 280.

certain aniline colours. The main purpose for which phosphorus is employed in the arts is, however, the manufacture of lucifer matches, for which purpose more than 1,000 tons are employed every year.

355 *Lucifer Matches.*—The application of this substance to the artificial production of heat and light is only of recent date. The oldest mode of artificially obtaining fire is that, still made use of by certain rude tribes, of rubbing together a piece of hard wood and a piece of soft wood, turning the former quickly on the latter until it takes fire. At a later time it was found that, when a piece of iron pyrites was struck with a mass of iron, sparks flew off, by means of which, dry inflammable materials, such as tinder, might be ignited. In place of iron pyrites flint was next used, and the iron replaced by a rough piece of steel. The tinder employed was made of charred linen, and the glowing tinder was made use of to ignite a match, consisting of a splint of wood, the ends of which were coated with sulphur. Up to the year 1827 this was the usual method employed for obtaining a light. The first lucifer matches consisted of pieces of wood the ends of which had been dipped into sulphur, and which were coated in addition with a mixture of sugar and potassium chlorate. In order to bring about the ignition of these matches, they were dipped into a bottle containing asbestos moistened with fuming sulphuric acid. Friction matches were invented in the year 1827, by John Walker, of Stockton, the material composing the inflammable mixture consisting of two parts of sulphide of antimony and one part of potassium chlorate, mixed together to a paste with gum and water. The matches, which had been previously coated with sulphur, were then dipped into this mixture and dried. In order to ignite them, these matches were drawn through two layers of sand-paper, held between the thumb and first finger. The antimony sulphide was soon replaced by phosphorus, and the first matches which were made in this way were sold in boxes containing from 50 to 60 for twopence. Potassium chlorate is now sometimes replaced by nitre, especially in the case of Continental makers, inasmuch as the latter substance is less liable to give rise to an explosive ignition. A further improvement consisted in the replacement of sulphur, which produces a disagreeable smell, by wax or paraffin.

The discovery of red phosphorus naturally led to the idea of the employment of this substance in the manufacture of lucifer matches, and this improvement was especially valuable, as, in spite of all care, the phosphorus disease made its appearance in match manufactories, where ordinary phosphorus was employed. The substitution of the red phosphorus for the white modification rendered its recurrence impossible.

Many difficulties had to be overcome in the employment of this new substance, and it was only after some time that the following mixture applied to the head of the matches was found to serve the required purpose:

Potassium Chlorate	32
Potassium Bichromate	12
Red Lead	32
Sulphide of Antimony	24

This mixture contains no phosphorus, and, as a rule, it will only ignite on a surface strewn with a mixture of amorphous phosphorus and sulphide of antimony. If, however, these so-called safety matches be quickly rubbed over a non-conducting surface such as that of glass or a smooth sheet of paper they can be made to take fire.

The use of ordinary phosphorus for friction matches has been forbidden in many countries, and matches which strike on any dry surface are now largely made in which the so-called phosphorus sesquisulphide, P_4S_3, or Schenck's scarlet phosphorus replaces the ordinary phosphorus. Such matches are less liable to accidental ignition and can be manufactured without causing serious poisoning of the workmen.

PHOSPHORUS AND HYDROGEN.

356 Three compounds of phosphorus with hydrogen are known—

1. Gaseous	Hydrogen	Phosphide	PH_3.
2. Liquid	„	„	P_2H_4.
3. Solid	„	„	P_4H_2.

Gaseous Hydrogen Phosphide or Phosphine, $PH_3 = 33{\cdot}77$.

By heating together phosphorus and caustic potash Gengembre in 1783[1] obtained a gas which was spontaneously inflammable.

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[1] *Crell. Ann.* **1**, 450.

Some years later Pelletier[1] and afterwards Davy[2] prepared a very similar gas by heating phosphorous acid. This gas differed, however, from the former, inasmuch as, although very easily inflammable, it did not take fire spontaneously on coming in contact with the air. Both compounds were at that time recognised to be compounds of hydrogen and phosphorus. The true explanation of the difference between these two gases was given by Paul Thénard.[3] He showed that the spontaneous inflammation of the one gas was due to the presence in it of small traces of the vapour of a liquid hydride of phosphorus.

Preparation.—(1) In order to prepare spontaneously inflammable phosphine, as the impure gas has been called, phosphorus is heated with milk of lime or with a solution of caustic potash. The spontaneously inflammable gas is evolved, and calcium or potassium hypophosphite left behind; thus:—

$$3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3.$$

(2) The same mixture of gases is also readily formed when phosphide of calcium is thrown into water.

Each bubble of the gas ignites, on coming to the surface of the water, with a sharp explosion, burning with a bright white flame, and a ring-like cloud of phosphorus pentoxide is formed, which on ascending shows the remarkable vortex motions. In order to exhibit this phenomenon, a small flask (*a* Fig. 154) is three-quarters filled with strong potash solution, a few pieces of phosphorus are thrown in, and the whole is gently warmed. As soon as small flames are seen at the mouth of the flask, a gas delivery-tube (*c*) is fixed in with cork, the lower end dipping under water.

When the spontaneously inflammable phosphine is exposed to the light, or when it is passed through a freezing mixture, or left in contact with carbon or potassium, it loses its power of spontaneous inflammability, inasmuch as the liquid hydride contained in it is either decomposed or condensed.

(3) The non-spontaneously inflammable phosphine is obtained by warming phosphorus with an alcoholic solution of potash, or by decomposing phosphide of calcium by means of hydrochloric acid.

(4) Phosphine may also be prepared by the action of dilute acids on the phosphides of zinc, iron, tin, or magnesium.[4]

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[1] *Crell. Ann.* 1796, ii. 148.

[2] *Phil. Trans.* 1809, i, 67.

[3] *Ann. Chim. Phys.* 1845 [3], **14**, 5.

[4] Lüpke, *Journ. Chem. Soc.* 1891, ii. 397.

The phosphine prepared by any of these methods is, however, not pure, but contains more or less hydrogen mixed with it. In order to obtain pure phosphine we make use of its property of combining with hydriodic acid to form the crystalline compound termed phosphonium iodide, PH_4I. This substance, when thrown into water, decomposes into its constituents, namely, phosphine, PH_3, and hydriodic acid, HI. The solid iodide, the preparation of which will be hereafter described, is employed as follows for the preparation of the pure gas.[1] Some pieces of the iodide of the size of peas, mixed with broken glass, are brought into a small flask. The flask is closed by a cork having two holes bored through it, in one of which is placed a stoppered funnel-tube, and in another a gas-delivery tube. The funnel is filled with concentrated solution of potash, and this is allowed to run into the flask slowly, when the following decomposition occurs:—

FIG. 154.

$$PH_4I + KOH = PH_3 + KI + H_2O.$$

According to Messinger and Engels[2] it is preferable to mix the phosphonium iodide with ether and gradually add water, a

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[1] **Hofmann**, *Ber*. 1871 **4**, 200.

[2] *Ber*. 1888, **21**, 326.

regular stream of phosphine being thus obtained. The gas prepared in this manner is not spontaneously inflammable, at any rate at the beginning of the operation, although if the evolution be carried on for a considerable length of time the spontaneously inflammable gas is formed (Rammelsberg).

Pure phosphine is also produced by the action of water or very dilute sulphuric acid on aluminium phosphide.[1]

Properties.—Phosphine is a colourless gas, smelling like rotten fish; it liquefies at −85°, solidifying at −133°·5 (Olszewski) and has the critical temperature 52·8° and the critical pressure 64 atmospheres.[2] The pure gas takes fire only above a temperature of 100°, but is so inflammable that the heat evolved by the friction of the stopper on opening the bottle containing the gas is sometimes sufficient to produce its inflammation. It may be mixed with oxygen without undergoing any alteration, but if this mixture be suddenly exposed to diminished pressure an explosion occurs. This remarkable phenomenon reminds one of the non-luminosity of phosphorus in pure oxygen and its luminosity in diluted oxygen at the same temperature.

Phosphine also takes fire when a few drops of dilute nitric acid are brought in contact with it, or when it is mixed with the vapours evolved from chlorine- or bromine-water. If the gas free from air be led through common nitric acid containing nitrous fumes, it becomes spontaneously inflammable, and it explodes in chlorine gas with great violence and with the evolution of a bright greenish-white light. Phosphine is somewhat soluble in water, and imparts to it a peculiar and disagreeable taste; the solution decomposes in the light with the evolution of hydrogen and the separation of red phosphorus. When a series of electric sparks is passed through the gas it also decomposes into phosphorus and hydrogen, the volume of the latter bearing to that of the original gas the proportion of three to two. In order to show this a eudiometer similar to the one already described (Fig. 130) may be employed, but instead of platinum wires pieces of gas-carbon are melted through the glass, inasmuch as platinum and phosphorus in contact unite, forming a silver white compound which is brittle and easily fusible (Hofmann).

Phosphine is absorbed by solutions of copper sulphate

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[1] Matignon, *Compt. Rend.* 1900, **130**, 1391.

[2] Leduc and Sacerdote, *Compt. Rend.* 1897, **125**, 397.

and mercuric chloride, phosphides of the metals being produced.[1]

It combines, like ammonia, with certain metallic chlorides: thus, for instance, with aluminium chloride $AlCl_3$, stannic chloride $SnCl_4$, titanium chloride $TiCl_4$, and antimony chloride $SbCl_5$.

Phosphine is a very poisonous gas, producing, when present in small proportions in respired air, in turn dyspnœa and death. It possesses the power of combining with the respiratory oxygen linked to hæmoglobin, but its toxic action appears to be almost entirely due to more complex operations.

357 *Phosphonium Compounds.*—Phosphine possesses feebly basic properties, and combines with hydrobromic acid and hydriodic acid to form salts, in a similar manner to ammonia.

FIG. 155.

These salts contain the compound radical PH_4, which is usually termed *phosphonium*, just as the compound radical NH_4 (p. 505) is termed ammonium.

Phosphonium Bromide, PH_4Br, crystallises in colourless cubes and boils at 30°. The vapour possesses a specific gravity of 1·906, so that we conclude that it is a mixture of phosphine and hydrobromic acid.

Phosphonium Iodide, PH_4I.—This beautiful compound, which crystallises in large transparent glittering quadratic prisms, can easily be obtained by placing in a retort of a litre capacity (see Fig. 155) 400 grams of common phosphorus, allowing an equal weight of dry carbon bisulphide to run in, and gradually adding 680 grams of pure iodine, care being taken to keep the retort

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[1] Joannis, *Compt. Rend.* 1898, **127**, 270; 1899, **128**, 1322, 1398; 1899, **129**, 336; Göttig, *Ber.* 1899, **32**, 1879.

well cooled. The carbon bisulphide is next completely removed by distillation in a water bath, and the retort connected with a long wide tube placed in a slightly slanting position, and furnished at its lower end with a tubulated receiver. This, again, is connected by a series of bulb tubes with two absorption-vessels, the first of which contains a dilute solution of hydriodic acid, and the second water. The object of this arrangement is to absorb the hydriodic acid formed during the reaction, and at the same time to prevent the liquid from entering the wide tube into which the phosphonium iodide is sublimed. The apparatus is then filled with pure carbon dioxide, a slow current of the gas being passed through during the operation. The experiment being thus far arranged, 240 grams of water are allowed to drop slowly by means of a stoppered tube-funnel into the retort, which is slightly warmed. The heat evolved by the action then taking place is sufficient to sublime the greater part of the phosphonium iodide into the wide tube. Towards the end of the operation, which usually requires about eight hours for its completion, the retort is heated somewhat more strongly. When no further increase in the amount of sublimate takes place, the apparatus is dismounted, the end of the long tube closed with corks, and the thick crust of phosphonium iodide loosened by means of a stout iron wire, and preserved in stoppered bottles.[1] The formation of phosphonium iodide is represented by the following equation:—

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4.$$

An excess of phosphorus is, in practice, employed because a part of this substance is converted, during the reaction, into the red modification. The formation of the hydriodic acid which escapes is due to the decomposition of the phosphonium iodide in the presence of warm water. Phosphonium iodide boils at about 80°, but it easily vaporises at a lower temperature. It is used in the laboratory as a powerful reducing agent, as well as for the preparation of many organic phosphorus compounds.

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[1] Hofmann, *Ber.* 1873, **6**, 286.

LIQUID HYDROGEN PHOSPHIDE $P_2H_4 = 65{\cdot}54$.

358 This substance, discovered by Thénard in the year 1845, is obtained by the action of water on calcium phosphide. The latter is prepared by the action of phosphorus on lime at a red heat and is best converted into liquid hydrogen phosphide by carefully adding it in small quantities at a time to water heated to 60°, the air in the apparatus having previously been displaced by hydrogen. The gas evolved is passed through a U-tube made of strong glass, 3 to 4 mm. in diameter, each of the limbs of which is furnished with a glass stopcock (Fig. 156). This tube is placed in a freezing mixture of pounded ice and salt and serves to condense the greater portion of the liquid phosphide, the remainder passing on with the gaseous hydride simultaneously formed. The liquid phosphide is colourless, has a specific gravity of about 1·01, boils at 57—58° under a pressure of 735 mm., and leaves no residue if not too strongly heated. It has the empirical formula PH_2, but its molecular formula is, in all probability, P_2H_4, corresponding to that of hydrazine, N_2H_4; no determination of its vapour density could, however, be made as it so readily undergoes decomposition.[1]

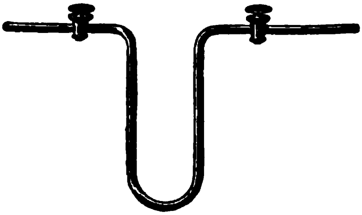

FIG. 156.

Liquid hydrogen phosphide is spontaneously inflammable, taking fire at once on exposure to the air and burning with a bright phosphorus-like flame. On exposure to light, or when heated above its boiling point, it decomposes into phosphine and solid hydrogen phosphide, according to the following equation:—

$$5P_2H_4 = 2P_2H + 6PH_3.$$

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[1] Gattermann and Hausknecht, *Ber.* 1890, **23**, 1174.

The same reaction takes place in contact with hydrochloric acid and hydriodic acid, 1 c.c. of hydrochloric acid being sufficient, according to Thénard, to decompose an indefinite quantity of the phosphide.

SOLID HYDROGEN PHOSPHIDE, $P_{12}H_6$.

359 This compound is formed in the manner already described and may be readily obtained by passing the uncondensed vapours obtained in preparing the foregoing compound into a large flask containing concentrated hydrochloric acid; it forms a yellow powder, having the empirical formula P_2H. The molecular formula[1] as determined from the freezing point of its solution in ordinary phosphorus is $P_{12}H_6$. When heated in a stream of carbon dioxide to 70° it decomposes into phosphorus and hydrogen, but does not take fire in the air until it attains a temperature of 160°.

It possesses feeble acid properties and unites with ammonia and piperidine to form black compounds,[2] which are also obtained by the action of these bases on scarlet phosphorus.

PHOSPHORUS AND THE HALOGENS.

360 *Phosphorus Trifluoride*, PF_3.—This compound is obtained by the action of copper phosphide on lead fluoride, or by allowing arsenic trifluoride to drop into phosphorus trichloride, moisture being excluded. It is a colourless gas which does not fume in the air, and condenses at $-10°$ under a pressure of 40 atmospheres to a colourless liquid, which boils at $-95°$ and solidifies at 160°.[3] It is only slowly absorbed by water, but forms an explosive mixture with oxygen, and unites with ammonia and bromine. The dry gas is dissociated by the passage of electric sparks into phosphorus and phosphorus pentafluoride.

Phosphorus Pentafluoride, PF_5, was discovered by Thorpe,[4]

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[1] Schenck, *Ber.* 1904, **37**, 915.

[2] Schenck, *Ber.* 1903, **36**, 4202. See also Stock, *Ber.* 1903, **36**, 1120; Dito, *Proc. akad. Amsterdam*, 1903, **6**, 1.

[3] Moissan, *Compt. Rend.* 1904, **138**, 789.

[4] *Proc. Roy. Soc.* 1877, **25**, 122.

who prepared it by the action of arsenic trifluoride on phosphorus pentachloride;

$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5.$$

It is also formed by heating phosphorus trifluorodibromide (p. 632), which splits up at 15° into the pentabromide and pentafluoride.[1] It is a colourless gas and decomposes in contact with water into phosphoric and hydrofluoric acids; it possesses a strongly irritating smell, and attacks the mucous membrane. It condenses to a liquid, which boils at $-75°$, and solidifies to a flocculent mass melting at $-83°$.[2] According to Thorpe, the gas is unaffected by passing a series of electric sparks through it whether alone or mixed with hydrogen or oxygen, whilst Moissan[3] found that with sparks of high tension a partial dissociation into fluorine and the trifluoride occurs. On the other hand, when phosphorus trifluoride comes in contact with free fluorine, it takes fire and burns with a yellow flame forming the pentafluoride. With dry ammonia it yields a white solid compound, having the composition $2PF_5,5NH_3$.

The vapour density of the compound is 63 ($H = 1$) and the molecular formula is therefore PF_5. The existence of this gaseous pentafluoride, taken in conjunction with its stability even at high temperatures, is of great theoretical interest, inasmuch as it shows that phosphorus can form pentavalent derivatives, capable of existing in a state of vapour.

361 *Phosphorus and Chlorine.*—Ordinary phosphorus takes fire in dry chlorine gas, and burns with a pale-greenish flame, with formation of phosphorus trichloride, PCl_3, or, with an excess of chlorine, phosphorus pentachloride, PCl_5.

Phosphorus Trichloride, PCl_3, was discovered by Gay-Lussac and Thénard in 1808. It is best prepared by placing red phosphorus in a retort (D, Fig. 157), and heating it whilst a stream of chlorine gas evolved in the flask (A), and dried by passing through the tube (C), is led over it.[4] The distillate is purified from any pentachloride which is formed by allowing it to remain in contact with ordinary phosphorus for some time and then rectifying.

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[1] Moissan, *Compt. Rend.* 1884, **99**, 655, 570; 1885, **100**, 272, 403.

[2] Moissan, *Compt. Rend.* 1904, **138**, 789.

[3] *Bull. Soc. Chim.* 1891, [3], **5**, 880.

[4] Dumas, *Ann. Chim. Phys.* 1859, [3], **55**, 172.

The trichloride is a mobile colourless liquid, which has a very pungent smell, boils at 76°, and does not solidify at $-115°$. The specific gravity of the liquid at 0° is 1·61294.[1] When exposed to the air it evolves white fumes, absorbing the atmospheric moisture, and decomposing into hydrochloric and phosphorous acids; thus:—

$$PCl_3+3H_2O=3HCl+P(OH)_3.$$

Water produces a similar reaction, but when only a small amount is used, about 0·05 per cent. of *phosphorous oxychloride*,

Fig. 157.

$POCl$, is produced. This is a yellowish solid, which is decomposed by water and is very hygroscopic; chlorine converts it into phosphoryl chloride, $POCl_3$.[2]

Sulphur trioxide acts violently on the trichloride with formation of phosphoric oxychloride and sulphur dioxide. Heated with concentrated sulphuric acid, chlorosulphonic acid and phosphorus pentoxide are produced according to the equation:

$$2PCl_3+3SO_2(OH)_2=2SO_2+5HCl+\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2+P_2O_5.$$

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[1] Thorpe, *Proc. Roy. Soc.* 1876, **24**, 295.

[2] Besson, *Compt. Rend.* 1898, **125**, 771.

It also unites with ammonia forming additive compounds.[1]

362 *Phosphorus Pentachloride*, PCl_5.—This compound was discovered by Humphry Davy in the year 1810, though it was first analysed by Dulong in 1816. It is easily formed by the union of phosphorus trichloride with chlorine. To prepare it, a current of dry chlorine is led through a wide tube on to the surface of the liquid trichloride contained in a flask surrounded by cold water. As the absorption of the chlorine is accompanied by the evolution of much heat, it is necessary to take care, in the beginning at least, that the liquid is well cooled. The reaction is finished as soon as the product assumes the condition of a perfectly dry mass.

Phosphorus pentachloride is a white or yellowish-white lustrous crystalline powder, possessing a very sharp unpleasant smell, and violently attacking the eyes and the mucous membrane. On heating, it is found to sublime below 100°, but it cannot be fused under the ordinary pressure of the atmosphere. When, however, it is heated under increased pressure, it melts at 148°, solidifying on cooling in transparent prisms. When heated still more strongly it boils, emitting a colourless vapour, which becomes coloured on further heating, the coloration increasing with the temperature. This is due to the fact that the vapour gradually undergoes dissociation into equal molecules of free chlorine and phosphorus trichloride. That this is the case is fully proved by Dumas' determination of the vapour density of this mixture at different temperatures:—

Temperature	182°	200°	250°	300°	336°
Density	73·3	70·0	57·6	52·4	52·5

These numbers clearly exhibit the gradual dissociation of the vapour, the density undergoing a continuous diminution until the temperature of 300° has been reached, above which point it remains constant. The vapour at these temperatures consists of a mixture of an equal number of molecules of the trichloride and chlorine, possessing the density: $\frac{136 \cdot 31 + 2 \times 35 \cdot 18}{4} = 51 \cdot 67$

That the vapour thus obtained contains free chlorine was proved by Wanklyn and Robinson[2] by allowing the vapour of the pentachloride to diffuse into an atmosphere of carbon dioxide. Chlorine gas being lighter than the vapour of the

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[1] Besson, *Compt. Rend.* 1890, **111**, 972.

[2] *Proc. Roy. Soc.* 1863, **12**, 507.

trichloride must diffuse more quickly than the latter. Accordingly, if, after the experiment, the vessels containing the pentachloride were found to contain the trichloride, whilst the atmosphere of carbon dioxide was admixed with free chlorine, the fact of dissociation would be proved. This was the result. The dissociation of the pentachloride may be prevented, or, at any rate, much diminished, by allowing it to volatilise in a space saturated with the vapour of the trichloride. Wurtz[1] obtained, under these circumstances, a vapour possessing a density close upon 103·3 (the normal density of PCl_5) at temperatures varying from 160° to 175°.

In perfectly dry air pentachloride of phosphorus undergoes no alteration; on exposure, however, to moist air, it decomposes with formation of phosphorus oxychloride; thus:—

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

This compound, as well as the pentachloride, dissolves in water with evolution of heat and formation of phosphoric and hydrochloric acids; the two reactions being:—

$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl,$$
$$PCl_5 + 4H_2O = PO(OH)_3 + 5HCl.$$

One of the most important properties of phosphorus pentachloride is its action on the acid-forming oxides and on the acids which it converts into the acid chlorides. Many examples of this kind of decomposition have already been given. For instance, it forms, with sulphur trioxide, the chloride of sulphuric acid or sulphuryl chloride; thus:—

$$SO_3 + PCl_5 = SO_2Cl_2 + POCl_3.$$

In this reaction two atoms of chlorine are replaced by one atom of oxygen. When, on the other hand, the pentachloride is allowed to act upon a hydroxy-acid, chlorine replaces the radical hydroxyl, OH; thus:—

$$SO_2\begin{cases}OH\\OH\end{cases} + PCl_5 = SO_2\begin{cases}Cl\\OH\end{cases} + POCl_3 + HCl.$$

In a similar way the pentachloride acts upon organic acids and other compounds containing hydroxyl; and in consequence of this property it is much used in the preparation of organic chlorides.

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[1] *Compt. Rend*, 1873, **76**, 601. See also Wegscheider, *Monatsh.* 1899, **20**, 307.

Phosphorus pentachloride forms a crystalline compound with iodine monochloride; thus:—PCl_5+ICl, as also with different metallic chlorides; thus:—PCl_5+FeCl_3, &c.

At the ordinary temperature ammonia acts upon phosphorus pentachloride with formation of chloramido-derivatives (p. 666); if, however, ammonia be passed into a cooled solution of the pentachloride in carbon tetrachloride, the two combine forming the additive compound $PCl_5,8NH_3$, which separates out as a white powder and is stable in the air.[1]

Phosphorus Trifluorodichloride, PF_3Cl_2, is formed by the direct combination of chlorine and phosphorus trifluoride, and is a colourless non-inflammable gas which is instantaneously absorbed and decomposed by water and alkalis. It has a vapour density of 5·4 (air = 1) corresponding with the above formula. It condenses to a liquid at −8° under atmospheric pressure, and is decomposed at 250° or by the passage of electric sparks into phosphorus pentafluoride and pentachloride. When treated with a small quantity of water it yields phosphorus oxyfluoride, POF_3, and with sulphur forms the corresponding thiofluoride,[2] PSF_3.

363 *Phosphorus Tribromide*, PBr_3.—Bromine and phosphorus act so violently upon each other that small pieces of phosphorus thrown upon bromine may cause a dangerous explosion. In order to prepare the tribromide, dry carbon dioxide is allowed to pass through bromine, a small portion of the vapour of which is carried over and is then brought into contact with dry phosphorus (Lieben). Another method of preparation consists in dissolving both of these elements separately in dry carbon bisulphide, and then gradually pouring the bromine solution into that containing the phosphorus and distilling. The tribromide can also be readily obtained by dropping bromine on to ordinary phosphorus which is covered by a layer of benzene.[3]

A simple process for preparing the tribromide is to place red phosphorus in a flask closed by a doubly-bored cork, one opening of which is connected with an inverted condenser, and round which cold water is allowed to flow, whilst through the second opening a funnel with glass stopcock is placed, by means of which bromine is allowed to fall slowly on the phosphorus. The first drops combine with evolution of

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[1] Besson, *Compt. Rend.* 1890, **111**, 972.

[2] Poulenc, *Compt. Rend.* 1891, **113**, 75.

[3] Christomanos, *Ber.* 1904, **37**, 2883.

light and heat, but this rapid combination soon ceases, and the bromine can be allowed to drop in without causing any violent action. The product is then separated by distillation from the excess of phosphorus which must be present (Schorlemmer).

The tribromide is a colourless mobile liquid boiling at 175°·3 (Pierre), 170°·8 (Christomanos[1]), solidifying at −41°·5 and possessing at 0° a specific gravity of 2·8847. It has a strong unpleasant pungent odour, and is decomposed in presence of water into phosphorous acid and hydrobromic acid.

Phosphorus Pentabromide, PBr_5.—This body is obtained when bromine is added to the cold tribromide. It is a lemon-yellow crystalline body which on heating melts, forming a red liquid which decomposes at 100° into the tribromide and bromine (Gladstone). When a current of carbon dioxide is led through the melted compound, the bromine is carried over and the tribromide remains behind. The pentabromide possesses an extremely pungent odour, and forms, when brought into contact with a small quantity of water, phosphorus oxybromide and hydrobromic acid.

When the pentabromide is mixed with bromine and sublimed in a sealed tube, red prisms of the *heptabromide*, PBr_7, are produced. These are converted by the tribromide into the yellow pentabromide, whilst water yields free bromine and the decomposition products of the pentabromide.[2]

364 *Phosphorus Trifluorodibromide*, PF_3Br_2, is obtained by the union of phosphorus trifluoride with bromine, and forms an amber yellow fuming liquid which solidifies at − 20°, forming pale yellow crystals (Moissan).

Phosphorus Chlorobromide, PCl_3Br_2.—If bromine and phosphorus trichloride are brought together in molecular proportions, heat is evolved and the liquid separates into two layers. The upper layer consists of a solution of bromine in phosphorus trichloride, whilst the lower consists of a solution of trichloride in bromine (Wichelhaus). If this mixture, placed in a sealed tube, be exposed for some weeks to a temperature of about 15°, a crystalline compound is formed which decomposes into its constituents at 35°.

Phosphorus chlorobromide combines with bromine and forms the compound $PCl_3Br_2 + Br_2$ which solidifies in large crystals, red by transmitted, but blue by reflected, light. A second compound,

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[1] *Zeit. anorg. Chem.* 1904, **41**, 276.

[2] Castle and Beatty, *Amer. Chem. J.* 1899, **21**, 322; 1900, **23**, 505.

$PCl_3Br_2+2Br_2$, is also formed at the same time, crystallising in needle-shaped crystals of a greenish lustre which soon turn brown. These compounds correspond to those formed by the union of phosphorus trichloride with iodine monochloride and with the metallic chlorides (Michaelis).

365 *Phosphorus Di-iodide*, P_2I_4.—This compound, which has an analogous composition to liquid hydrogen phosphide, is obtained by dissolving one part of phosphorus in carbon bisulphide and then adding gradually 8·2 parts of iodine. On gently warming the solution so as to distil off the carbon bisulphide the di-iodide remains behind as a yellow crystalline mass. When the bisulphide is cooled down to 0°, the same compound separates out in long orange-red crystals (Corenwinder). The crystals melt at 110° and are decomposed by water with formation of red phosphorus, phosphorous acid, and hydriodic acid; thus:—

$$3P_2I_4+12H_2O=2P+4P(OH)_3+12HI.$$

Its vapour density corresponds to the formula P_2I_4.[1]

Phosphorus Tri-iodide, PI_3, is obtained in a similar way to the foregoing, but using 1½ times as much iodine. By gently heating the solution, the greater portion of the bisulphide of carbon is got rid of, and the residue is cooled down by a mixture of salt and ice. Red six-faced crystals separate out which melt at 61° and on gently cooling may be obtained of large size. The iodide may also be prepared by the action of hydrogen iodide on phosphorus trichloride,[2] and is formed when potassium iodide is heated with phosphorus trichloride.[3] On the addition of water to this compound hydriodic and phosphorous acids are formed; thus:—

$$PI_3+3H_2O=P(OH)_3+3HI.$$

It is reduced by mercury to the di-iodide.

Phosphorus Pentiodide, PI_5, has been described by Hampton,[4] but its existence cannot as yet be regarded as definitely proved.

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[1] Troost, *Compt. Rend.* 1882, **95**, 293.

[2] Besson, *Compt. Rend.* 1897, **124**, 1346.

[3] Snape, *Chem. News*, 1896, **74**, 27.

[4] *Chem. News*, 1880, **42**, 180.

OXIDES AND OXYACIDS OF PHOSPHORUS.

366 Oxygen forms with phosphorus three well-defined compounds and with hydrogen and oxygen a large number of acids :—

Phosphorous oxide, P_4O_6.	Hypophosphorous acid, H_3PO_2.
Phosphorus tetroxide, P_2O_4.	Phosphorous acid, H_3PO_3.
Phosphorus pentoxide, P_4O_{10}.	Hypophosphoric acid, $P_2O_2(OH)_4$.
	Phosphoric acid, $PO(OH)_3$.
	Pyrophosphoric acid, $P_2O_3(OH)_4$.
	Metaphosphoric acid, PO_2OH.

367 The existence of a suboxide, P_4O, has been maintained by some chemists and denied by others. The substance to which this formula has been given was first obtained by Leverrier by allowing a solution of phosphorus in phosphorus trichloride to oxidise in the air,[1] and is also obtained by the action of zinc on phosphorus oxychloride,[2] and together with the other oxides when phosphorus is burned in an insufficient supply of air.[3] It is also formed when ordinary phosphorus is dissolved in alcoholic potash and the dark red solution precipitated by a dilute acid, and when a hypophosphite is treated with acetic anhydride.[4] It is a yellow to red substance, and closely resembles red phosphorus in appearance and properties. The compound has never been prepared free from hydrogen, and is probably simply red phosphorus containing more or less impurity, of the nature of the oxides or acids of phosphorus.[5]

HYPOPHOSPHOROUS ACID, H_3PO_2.

368 The salts of this acid were discovered by Dulong in 1816. They are formed when the phosphides of the metals of the

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[1] *Annalen*, 1838, **27**, 167.

[2] Reinitzer and Goldschmidt, *Ber.* 1880, **13**, 847.

[3] Thorpe and Tutton, *Journ. Chem. Soc.* 1890, 549; 1891, 1019.

[4] Michaelis and Pitsch, *Ber.* 1899, **32**, 327; *Annalen*, 1899, **310**, 45; Michaelis and Arendt, *Annalen*, 1901, **314**, 259; 1902, **325**, 361.

[5] Chapman and Lidbury, *Journ. Chem. Soc.* 1899, 973; Burgess and Chapman, *Journ. Chem. Soc.* 1901, 1235; Browning, *Proc. Chem. Soc.* 1901, 243. See also Biltz, *Ber.* 1894, **27**, 1257; Besson, *Compt. Rend.* 1897, **124**, 763; 1897, **125**, 1032; 1901, **132**, 1556.

alkaline earths are decomposed by water, or when phosphorus is boiled with an alkali or an alkaline earth. For the purpose of preparing the acid, baryta is best employed, as it is from the barium salt that not only the other salts but also the free acid are easily prepared. The formation of barium hypophosphite is shown in the following equation:—

$$3Ba(OH)_2 + 8P + 6H_2O = 3Ba(PH_2O_2)_2 + 2PH_3.$$

At the same time a small quantity of barium phosphate is formed, but this can readily be separated from the hypophosphite by filtration. To the clear solution, the requisite quantity of dilute sulphuric acid is added, and the filtered solution evaporated to a syrupy consistency. On cooling the solution, the hypophosphorous acid is obtained in the form of a thick, very acid liquid. Hypophosphorous acid can also be obtained in the form of a white crystalline mass as follows.[1] The tolerably concentrated solution is gently evaporated in a platinum dish at a temperature below its boiling point and then gradually heated from 110° up to 130°, at which temperature it is allowed to remain for ten minutes. The solution thus obtained is cooled, poured into a stoppered bottle, and this placed in a freezing mixture at a few degrees below 0°. The acid is then found either to crystallise spontaneously or to do so on being touched with a glass rod.

Hypophosphorous acid can also be prepared by decomposing the sodium salt with concentrated sulphuric acid, extracting with alcohol, and evaporating in vacuo. When dried over phosphoric oxide it melts at 26·5°.

Hypophosphorous acid, when strongly heated, decomposes into phosphine and phosphoric acid; thus:—

$$2H_3PO_2 = PH_3 + H_3PO_4;$$

but the reaction occurs in two stages, phosphorous acid being formed as an intermediate product (Marie). Its aqueous solution precipitates gold and silver from solutions of their salts, phosphoric acid being formed; thus:—

$$4AgNO_3 + 2H_2O + H_3PO_2 = 4Ag + 4HNO_3 + H_3PO_4.$$

When a solution of this acid is added to mercuric chloride solution, either calomel (mercurous chloride) or metallic mercury

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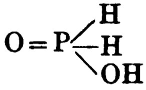
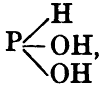
[1] Thomsen, *Ber.* 1874, **7**, 994, 996.

[2] Marie, *Compt. Rend.* 1904, **138**, 1216.

is precipitated, according to the proportions in which the acid is present.

Hypophosphorous acid is also oxidised by chlorine, iodine, and other oxidising agents to phosphoric acid, and when exposed to the air it takes up oxygen with the formation of phosphorous acid. Nascent hydrogen reduces it to phosphine. Hypophosphorous acid is a monobasic acid, although it contains 3 atoms of hydrogen, and it is therefore probable that its constitution is  $\mathrm{O{=}P}\begin{array}{l}\diagup \mathrm{H}\\ -\mathrm{H}\\ \diagdown \mathrm{OH}\end{array}$, although the constitution,  $\mathrm{P}\begin{array}{l}\diagup \mathrm{H}\\ -\mathrm{OH}\\ \diagdown \mathrm{OH}\end{array}$, according to which it is a dihydroxylphosphine, is accepted by some chemists.

The Hypophosphites.—Most of the salts of hypophosphorous acid are soluble in water, some being also soluble in alcohol, and crystallisable. In the dry state they do not undergo alteration in the air and may be boiled in water, free from absorbed oxygen, without decomposition. Like the free acid, all the hypophosphites possess strong reducing properties, giving with solutions of gold, silver, and mercury the same reactions as the acid itself.

PHOSPHOROUS OXIDE OR PHOSPHOROUS ANHYDRIDE, P_4O_6.

369 This oxide was first obtained by Sage in 1777, and was also observed by Cabell, but was first thoroughly examined by Thorpe and Tutton.[1] In order to prepare it the apparatus shown in Fig. 158 is employed. Pieces of phosphorus about an inch in length are placed in the wide combustion tube (*a*), which is open at one end to admit air and bent into the shape shown to prevent escape of melted phosphorus. The other end of the tube is fitted into a brass tube enclosed in a second wider brass tube (*b*), water being introduced into the space between the tubes by means of *d*. A loose plug of glass wool is placed at the further end of the brass tube before the connection with the U-shaped condenser (*c*), surrounded by ice and salt, which is in turn connected with the wash bottle (*f*) containing sulphuric acid. The outlet *f* is in connection with a water pump, by means of which a slow current of air is drawn

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[1] *Journ. Chem. Soc.* 1890, 549; 1891, 1019.

through the apparatus. The phosphorus is ignited by carefully heating, and the temperature of the water in the jacket allowed to reach 50° and maintained at that temperature till nearly the end of the experiment, when it is allowed to rise to 60°. The red oxide formed condenses in the portion of the tube nearest the phosphorus, and the passage of the pentoxide is prevented by the plug of glass wool, whilst the phosphorous oxide passes through to the condenser. The reaction is stopped as soon as four-fifths of the phosphorus has been burnt, and the U tube detached and warmed, when the phosphorous oxide melts and falls into the small bottle below.

Phosphorous oxide is thus obtained as a wax-like mass, but may also be condensed in the form of feathery crystals, and when the melted substance is allowed to cool it separates out in thin prisms capped by pyramids, probably belonging to th monoclinic system. It has an unpleasant garlic-like odour, melts at 22°·5, and resolidifies at 21°, but frequently exhibits the property of superfusion; the liquid has a specific gravity of 1·9358 at 24·8°/4°. It boils at 173°·1 (corr.) in an atmosphere of nitrogen, its vapour density being 7·74; its molecular formula, like that of the corresponding oxide of arsenic, is therefore P_4O_6. When quite pure it is unaltered in the light, but it usually assumes a dark red colour owing to the separation of red phosphorus.

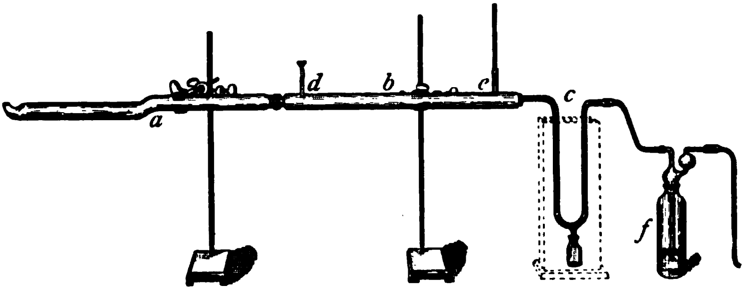

FIG. 158.

Phosphorous oxide is only attacked very slowly by cold water, with the gradual formation of phosphorous acid; with hot water, however, a violent reaction takes place, spontaneously inflammable hydrogen phosphide being evolved, and phosphoric acid and either red phosphorus or the suboxide remaining behind. On exposure to the air or oxygen it spontaneously oxidises to phosphorus pentoxide, and when heated to 50—60° ignites and burns with great brilliancy. It is acted upon with great violence by alcohol, ignition taking place, but dissolves without alteration in ether, carbon bisulphide, benzene, or chloroform. When heated in a sealed tube to 210° it becomes turbid, and at 440° is completely converted into red phosphorus and phosphorus tetroxide. When thrown into chlorine it burns with a green flame, but by the slow action of the gas it yields a mixture of phosphoryl and metaphosphoryl chlorides. With sulphur it yields phosphorus sulphoxide, and with ammonia the diamide of phosphorous acid, $HO \cdot P(NH_2)_2$.

PHOSPHOROUS ACID, H_3PO_3.

370 This acid is formed together with hypophosphorous and phosphoric acids when phosphorus is oxidised in moist air. In order to prepare pure phosphorous acid the reaction employed by Davy in 1812 is employed. This consists in the decomposition of the trichloride by water; thus:—

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl.$$

For this purpose it is not necessary to prepare the pure trichloride separately, for, if chlorine be led through melted phosphorus under water, the trichloride is first formed and, on coming in contact with the water, this is decomposed as shown in the above equation. Care must be taken to stop passing the chlorine in before all the phosphorus has disappeared, as the chlorine would otherwise oxidise the phosphorous to phosphoric acid. It is difficult to prevent this altogether even if phosphorus is present in excess.

By evaporating the solution until the residue attains a temperature of 180° a thick syrupy substance is obtained which is transformed more or less rapidly on cooling into a crystalline mass melting at 70°·1.[1] Phosphorous acid has an acid, garlic-like taste, absorbs moisture rapidly from the air, and deliquesces. When strongly heated, it decomposes into phosphine and phosphoric acid; thus:—

$$4H_3PO_3 = 3H_3PO_4 + PH_3,$$

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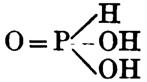
[1] J. Thomsen, *Ber.* 1874, 7, 996.

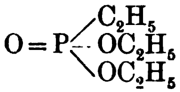
and when treated with phosphorus pentachloride, phosphorus trichloride and oxychloride are formed:—

$$P(OH)_3 + 3PCl_5 = PCl_3 + 3POCl_3 + 3HCl.$$

Hence the trichloride is the chloride of phosphorous acid.[1]

The aqueous solution of the acid also slowly absorbs oxygen from the air, and in presence of nascent hydrogen it is reduced to phosphine. It acts as a strong reducing agent, precipitating gold, silver, and mercury from their solutions like hypophosphorous acid, and being slowly oxidised by iodine and by potassium permanganate.

The Phosphites.—Although a weak acid, phosphorous acid is tribasic, but under ordinary circumstances only two atoms of its hydrogen can be replaced by metals. A normal tribasic salt, $P(ONa)_3$, is known, but this has not yet been obtained in the anhydrous state.[2] These facts seem to indicate that the constitution of the acid is  $O=P\begin{cases}H\\OH\\OH\end{cases}$, whilst its formation from the trichloride and its reducing properties point to the formula $P(OH)_3$. Isomeric ethers[3] are known, as in the case of nitrous and sulphurous acids, of the formulæ



$$O=P\begin{cases}C_2H_5\\OC_2H_5\\OC_2H_5\end{cases} \quad \text{and} \quad P(OC_2H_5)_3.$$

No experimental method of deciding between the two formulæ has as yet been found.

The phosphites which are soluble in water possess an acid and garlic-like taste. They act upon the salts of the noble metals like the hypophosphites, from which, however, they are distinguished by giving a precipitate with baryta- or lime-water.

Pyrophosphites such as $Na_4P_2O_5$ also exist and the corresponding *pyrophosphorous acid*, $H_4P_2O_5$, has been obtained[4] by the action of phosphorus trichloride on phosphorous acid, as a mass of deliquescent crystals melting at 38°.

[1] Geuther, *J. pr. Chem.* 1873, [2], **8**, 359.
[2] Zimmermann, *Annalen*, 1875, **175**, 21.
[3] Michaelis and Becker, *Ber.* 1897, **30**, 1003.
[4] Auger, *Compt. Rend.* 1903, **136**, 814.

PHOSPHORUS TETROXIDE OR PHOSPHOROSOPHOSPHORIC OXIDE, $(PO_2)_n$.

371 This compound is prepared by heating the mixture of oxides obtained by the combustion of phosphorus in an insufficient supply of air to 290° in a sealed tube. Phosphorus tetroxide then volatilises and condenses in the cool portions of the tube, in the form of clear transparent crystals, belonging to the rhombic system, of the specific gravity 2·537 at 22·6°/4°.

It may also be prepared from phosphorous oxide by heating it to 440°, when it decomposes into red phosphorus and phosphorus tetroxide.

The tetroxide is a deliquescent substance and dissolves in water with evolution of heat yielding a strongly acid solution which is unaltered by boiling, reduces mercuric to mercurous chloride, and gives with silver nitrate a white precipitate rapidly changing to black. It only decolorises permanganate solution slowly, and on evaporation in vacuo yields a thick colourless syrup containing phosphorous and phosphoric acids. It is not the anhydride of hypophosphoric acid, as the latter reduces permanganate quickly, and also forms a sparingly soluble sodium salt, which cannot be obtained from the solution of the tetroxide.[1]

The vapour density[2] at about 1400° is 230, corresponding with a molecular weight somewhat less than that required by the formula P_8O_{16}.

HYPOPHOSPHORIC ACID, $H_4P_2O_6$.

372 It was formerly supposed that the acid obtained by the slow oxidation of phosphorus in moist air, prepared by exposing thin strips of phosphorus to a limited supply of moist air as shown in Figs. 159 and 160, was phosphorous acid. Salzer[3] has, however, shown that in addition to phosphoric and phosphorous acids this liquid contains hypophosphoric acid. On neutralising with caustic soda, a slightly soluble salt, sodium hypophosphate, $H_2Na_2P_2O_6$, separates out. A solution of this salt yields with lead acetate an insoluble salt, $Pb_2P_2O_6$, from which, on decomposition with sulphuretted hydrogen, the acid can be prepared

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[1] Thorpe and Tutton, *Journ. Chem. Soc.* 1886, 833.

[2] West, *Journ. Chem. Soc.* 1902, 923.

[3] *Annalen*, 1877, **187**, 222; 1878, **194**, 28; 1882, **211**, 1.

as an odourless acid liquid. The aqueous solution decomposes on concentration. Hypophosphoric acid is tetrabasic, and yields two classes of well defined salts. The sodium salts crystallise well:

$Na_4P_2O_6+10H_2O$	Normal sodium hypophosphate.
$H_2Na_2P_2O_6+9H_2O$	Hydrogen sodium hypophosphate.

Phosphorus Pentoxide, Phosphoric Oxide or Phosphoric Anhydride, P_4O_{10}.

373 The thick white clouds which are formed when phosphorus burns brightly in the air consist of this oxide. If a small piece of phosphorus is burnt on a dry plate covered with a bell-jar, these fumes condense partly on the sides of the glass and partly on the plate, in the form of a white flocculent powder, whilst the portion near the burning phosphorus forms a glassy mass. This white powder is amorphous, and may be sublimed in a test-tube heated over a gas lamp, yielding a crystalline sublimate, which changes back to an amorphous powder at 440°. Both of these forms become vitreous when heated to incipient redness under pressure. The changes from crystalline to amorphous, and from amorphous to vitreous are accompanied by evolution of heat.[1] The pure powder is perfectly colourless and odourless. If it should possess any garlic-like smell it contains phosphorous oxide, and if it has a yellowish or reddish colour it is mixed with red phosphorus. In order to free phosphorus pentoxide

Fig. 159.

Fig. 160.

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[1] Hautefeuille and Perrey, *Compt. Rend.* 1884, **99**, 33; Giran, *Compt. Rend.* 1903, **136**, 550.

from all traces of lower oxides, it must be distilled over platinum sponge in a current of oxygen, until the product no longer reduces a solution of silver nitrate.[1]

The density of the vapour is 162 ($H=1$) at about 1000° and 150 at about 1400°, a value which is slightly higher than corresponds with the molecular formula P_4O_{10}.[2]

It possesses no action upon dry blue litmus paper, and is excessively hygroscopic, deliquescing very quickly when exposed to the air, with formation of metaphosphoric acid:—

$$P_4O_{10} + 2H_2O = 4HPO_3.$$

When thrown into water it dissolves with a hissing noise and with the evolution of a large amount of heat. On heating with carbon, or other reducing agents, phosphorus is formed:—

$$P_4O_{10} + 10C = P_4 + 10CO.$$

Phosphorus pentoxide is often used in the laboratory as a desiccating agent, especially for the purpose of removing the last traces of moisture from gases or from liquids. According to Morley[3] a gas dried by passage over phosphoric oxide does not contain more than 1 mgrm. of water vapour in 40,000 litres, whilst sulphuric acid leaves about 1 mgrm. of water vapour in every 400 litres. Owing to its power of combining with water it is able to withdraw the elements of water from many compounds containing oxygen and hydrogen. Thus it is used for the preparation of nitrogen pentoxide and other compounds.

In order to prepare larger quantities of the pentoxide the arrangement shown in Fig. 161 is employed. (A) is a large dry glass balloon, provided with three necks (*a*, *d*, and *g*); the neck (*g*) is connected with a powerful water-aspirator by means of which air, dried by passing through the drying tube (*f*), is drawn into the balloon; *g* communicates with a large wide-necked bottle (B) into which a portion of the light powder is driven by the current of air; through the neck (*a*) passes a straight glass tube closed with a cork at the top but open at the bottom, reaching nearly to the centre of the balloon and having a small copper crucible (*c*) fixed to its lower end. A piece of phosphorus is

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[1] Threlfall, *Phil. Mag.* 1893; Shenstone and Beck, *Journ. Chem. Soc.* 1893, 473.

[2] Tilden and Barnett, *Journ. Chem. Soc.* 1896, 154; West, *Journ. Chem. Soc.* 1902, 923.

[3] *Amer. J. Sci.*, 1887, **34**, 200.

dropped down the straight tube into the crucible and ignited by a hot wire, a good current of air being kept up until the operation is complete; a second piece of phosphorus is then dropped down into the crucible (*c*), and when this is burnt a third piece is introduced, and so on, until a sufficient quantity of the pentoxide has been obtained.

A more practically useful arrangement for preparing the pentoxide in quantity consists of a cylinder (*a*, Fig. 162), open at both ends, made of common sheet-iron, fourteen inches high and twelve inches in diameter, having a cover provided with a bent chimney (*b*), one inch in diameter, closed by a cork. The cylinder is supported by a wooden tripod, and rests in a sheet-iron funnel (*h*), fitting into the neck of a wide-mouthed bottle (*g*). A copper spoon (*d*), fixed to an iron rod, serves to receive the phosphorus which is from time to time renewed by drawing back the spoon to the opening (*e*) and dropping in a fresh piece. In order to renew the supply of air, which during dry weather does not require desiccation, the board (*i*) is occasionally removed, and air allowed to enter between the funnel and the

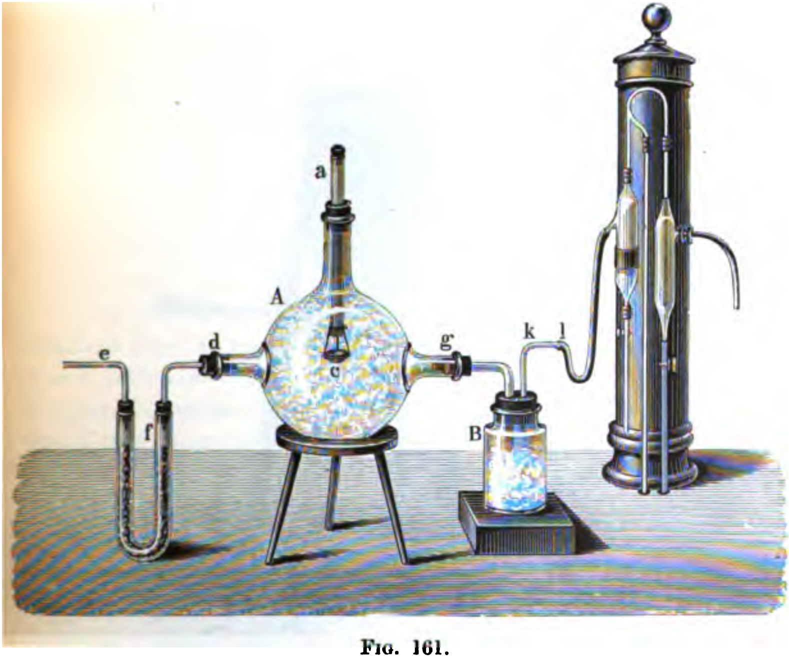

FIG. 161.

cylinder.[1] On account of its being so exceedingly hygroscopic the pentoxide thus obtained must be preserved in well-stoppered bottles, or, better, in hermetically-sealed flasks.

PHOSPHORIC ACID.

374 The history of this acid possesses a peculiar interest for the scientific chemist. In the year 1746, Marggraf observed that, when *fusible salt of urine*, NH_4NaHPO_4, is mixed with a solution of silver nitrate, a yellow-coloured silver salt is precipitated. It was afterwards noticed that other salts of phosphoric acid, as, for instance, the ordinary phosphate of soda, gave the same reaction; but Clark, in the year 1828, pointed out that when the salt is heated and then dissolved in water, the solution thus obtained gives with silver nitrate a white precipitate. He, therefore, distinguished the acid contained in

FIG. 162.

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[1] V. Grabowski, *Annalen*, 1865, **136**, 119.

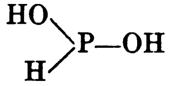
the heated salt from that contained in the common phosphate, and termed the former pyrophosphoric acid. In 1829 Gay-Lussac proved that the acid thus prepared can be converted into other salts without losing its peculiar properties; and Berzelius and Engelhardt had previously found that a freshly prepared solution of well-ignited phosphoric acid is able to coagulate clear solutions of albumen, whilst this is not the case when the solution of the acid has been standing for any considerable length of time. These and similar observations led to the conclusion that phosphoric acid, with which the pentoxide was then classed, can exist in several isomeric conditions.

The classical researches of Thomas Graham[1] first threw a clear light on this subject. He showed, in the first place, that, in addition to ordinary phosphoric acid and pyrophosphoric acid, a third modification exists, to which he gave the name of metaphosphoric acid, and that this is the substance which has the power of coagulating albumen. He also ascertained that common phosphates, when they are saturated with a base, contain three times as much of that base, in proportion to the same weight of phosphoric acid as the metaphosphates, whilst the pyrophosphates contain twice as much as the metaphosphates. Graham likewise proved that, when the acids are liberated from these different salts, they may be regarded as containing different quantities of water. Hence the composition of the three acids is as follows:—

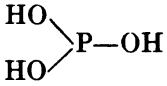
	Old notation.	New notation.
Common, or Orthophosphoric acid	$P_2O_5 + 3H_2O$	H_3PO_4
Pyrophosphoric acid	$P_2O_5 + 2H_2O$	$H_4P_2O_7$
Metaphosphoric acid	$P_2O_5 + H_2O$	HPO_3.

The exact constitution of these acids has been the subject of a considerable amount of discussion. The supporters of the theory of the constant valency of the elements regarded these three acids as well as hypophosphorous and phosphorous acids as derivatives of phosphine, PH_3, and ascribed to them the following constitutional formulæ:

Hypophosphorous Acid.



Phosphorous Acid.



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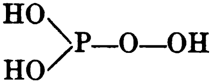
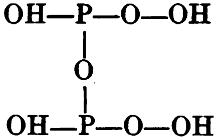
[1] *Phil. Trans.* 1833, **2**, 253.

Orthophosphoric Acid.

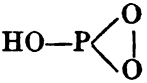


Pyrophosphoric Acid.



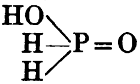
$$\begin{array}{c}\mathrm{OH{-}P{-}O{-}OH}\\ |\\ \mathrm{O}\\ |\\ \mathrm{OH{-}P{-}O{-}OH}\end{array}$$

Metaphosphoric Acid.

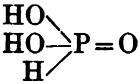


Other chemists, however, believed that in these acids phosphorus behaves as a pentad, and represented them by the following formulæ:

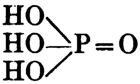
Hypophosphorous Acid.



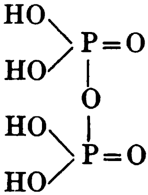
Phosphorous Acid.



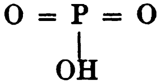
Orthophosphoric Acid.



Pyrophosphoric Acid.



Metaphosphoric Acid.



$$\begin{array}{c}\mathrm{O = P = O}\\ |\\ \mathrm{OH}\end{array}$$

Since it has been shown that phosphorus forms a stable pentafluoride, the vapour density of which remains constant through a considerable range of temperature and corresponds to the molecular formula PF_5, the pentad nature of phosphorus in many of its derivatives has been generally admitted, and the second series of formulæ for the phosphorus acids is now almost universally accepted.

According to these formulæ, moreover, the basicity of each acid corresponds with the number of hydroxyl groups present.

Poisonous Action of the Acids of Phosphorus.—When administered in an uncombined condition, the various oxides of phosphorus produce apparently the same symptoms which follow the administration of other mineral acids. Sufficient data do not exist as to the specific physiological action of all these compounds.

In the case of ortho- meta- and pyrophosphoric acids it would appear that the first, when in combination with inactive bases, acts as a perfectly inert body. The second possesses some activity as a poison, while the pyro-salts when introduced directly into the blood are found to be very powerful poisons (Gamgee).

ORTHOPHOSPHORIC ACID, H_3PO_4.

375 In order to prepare this acid, red phosphorus is heated in a retort with common concentrated nitric acid. The phosphorus is oxidised at the expense of the nitric acid, and red fumes are slowly evolved. When the phosphorus has dissolved, the residue is evaporated in a porcelain dish, and the concentrated solution repeatedly treated with nitric acid, in order to oxidise completely any phosphorous acid which may have been formed. As soon as the further addition of nitric acid is unaccompanied by the evolution of red fumes, the operation is concluded, and the residue only requires to be evaporated again, in order to get rid of the excess of nitric acid (v. Schrötter). Common phosphorus was formerly employed instead of red phosphorus for this purpose; but this undergoes oxidation much more slowly than the red variety, inasmuch as it melts forming round globules, which are only slowly attacked by the nitric acid. In addition to this, when common phosphorus is employed, weak nitric acid can alone be used, as the strong acid is apt to produce an explosion when brought in contact with it.

The residue obtained in the preparation of hydriodic acid by means of iodine and phosphorus consists of a mixture of phosphoric and phosphorous acids, containing a small quantity of hydriodic acid. In order to prepare pure orthophosphoric acid from this residue, it may be heated with a little fuming nitric acid, and filtered, to separate it from the solid iodine which is liberated. More nitric acid is then added, in order to oxidise the phosphorous acid, and the liquid is evaporated to a syrupy consistency.

Orthophosphoric acid is prepared on the large scale from bone-ash, which consists chiefly of tri-calcium phosphate, together with a small quantity of magnesium phosphate and calcium carbonate. According to Liebig, equal weights of sulphuric acid and bone-ash are taken; the sulphuric acid is diluted with ten times its weight of water, and is allowed to remain in contact with the bone-ash for some time. The acid solution is then filtered through linen, and the filtrate evaporated to a small bulk. On the addition of strong sulphuric acid, the calcium, still present in solution, is precipitated as gypsum. The clear solution is then poured off, evaporated to dryness, and freed from an excess of sulphuric acid by ignition.

The residue is free from lime and sulphuric acid, but it contains small quantities of magnesia, which can only with difficulty be removed.

In order to prepare a pure acid from bone-ash, the powdered ash is dissolved in the smallest possible quantity of nitric acid, and to the clear liquid a solution of lead acetate is added. A precipitate of lead phosphate falls down, which must be warmed for some time with the liquid, in order to free the precipitate from any calcium phosphate which is thrown down with the lead salt. It is well washed with boiling water, and decomposed by sulphuretted hydrogen. According to Berzelius's method, the lead salt is decomposed by dilute sulphuric acid, and the excess of acid removed by ignition of the evaporated filtrate. The residue is then dissolved in water and freed from traces of lead by sulphuretted hydrogen.

Another method which may be employed is to dissolve the bone-ash in its own weight of hydrochloric acid of specific gravity 1·18, diluted with four times its weight of water. To this solution one-and-a-half parts of dry sodium sulphate are added, whereby a precipitate of gypsum is produced; this is then filtered off, and the boiling solution neutralised with sodium carbonate; the solution is again filtered, to separate any calcium carbonate which may fall down, and the whole precipitated with barium chloride. The precipitate thus formed consists of a mixture of barium sulphate and barium phosphate and this is decomposed by one part of sulphuric acid, having a specific gravity of 1·71 (Neustadt).

A further method is to treat calcium phosphate with hydrofluoric acid in a leaden dish; the excess of acid is then evaporated off and the solution filtered from separated calcium fluoride and evaporated.[1]

Commercial phosphoric acid frequently contains arsenic acid, derived from the sulphuric acid or hydrochloric acid employed in its manufacture. In order to free it from arsenic, it must be dissolved in water, sulphur dioxide led through the warm solution, in order to reduce the arsenic acid to arsenious acid, then the solution boiled to remove the excess of sulphur dioxide, and sulphuretted hydrogen passed through, by which means the whole of the arsenic is precipitated as the insoluble trisulphide.

376 Phosphoric acid is extremely soluble in water; it has a pleasant purely acid taste, and is perfectly free from smell.

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[1] Nicolas, *Compt. Rend.* 1890, **111**, 975.

When the aqueous acid is evaporated down until the residue possesses the composition H_3PO_4, it presents the appearance of a thick syrup, from which, on standing, a crystalline mass is deposited. If a crystal of this acid be dropped into a freshly-prepared solution of the requisite strength, crystals begin to form at once, and soon spread throughout the mass. These crystals belong to the rhombic system, forming six-sided prisms terminated by six-sided pyramids, and melt at 38·6°.[1] The crystallised acid may be heated to 160° without undergoing any alteration, but above this temperature it loses water, and at 230–235° is completely converted into pyrophosphoric acid, $H_4P_2O_7$. This substance, in its turn, loses water at about 290°, and when heated to redness, is completely converted into metaphosphoric acid, HPO_3.[2]

The table below gives the variation of the specific gravity with the percentage composition of aqueous solutions of orthophosphoric acid:—[3]

Specific Gravity.	Per Cent. P_2O_5.	Specific Gravity.	Per Cent. P_2O_5.	Specific Gravity.	Per Cent. P_2O_5.
1·508	49·60	1·328	36·15	1·144	17·89
1·492	48·41	1·315	34·82	1·136	16·95
1·476	47·10	1·302	33·49	1·124	15·64
1·464	45·63	1·293	32·71	1·113	14·33
1·453	45·38	1·285	31·94	1·109	13·25
1·442	44·13	1·276	31·03	1·095	12·18
1·434	43·95	1·268	30·13	1·081	10·44
1·426	43·28	1·257	29·16	1·073	9·53
1·418	42·61	1·247	28·24	1·066	8·62
1·401	41·60	1·236	27·30	1·056	7·39
1·392	40·86	1·226	26·36	1·047	6·17
1·384	40·12	1·211	24·79	1·031	4·15
1·376	39·66	1·197	23·23	1·022	3·03
1·369	39·21	1·185	22·07	1·014	1·91
1·356	38·00	1·173	20·91	1·006	0·79
1·347	37·37	1·162	19·73		
1·339	36·74	1·153	18·81		

Orthophosphoric acid in aqueous solution is a comparatively weak acid and at moderate dilutions yields mainly the two ions

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[1] J. Thomsen, *Ber.* 1874, **7**, 997.

[2] Watson, *Chem. News*, 1893, **68**, 199.

[3] John Watts, *Chem. News*, 1865, **12**, 160.

$\overset{+}{H}$ and $H_2\overset{-}{PO_4}$. Only at extreme dilutions or in presence of two equivalents of a base is the trivalent ion $\overset{---}{PO_4}$ produced and then only to a very slight extent. In other words, the acid function of the third hydrogen atom is very feeble, that of the second being somewhat greater, and that of the first again greater. The reactions of the alkali salts in solution are in full agreement with these conditions (Vol. II. (1897) p. 88).

377 *The Orthophosphates.*—Orthophosphoric acid, being tribasic, forms three classes of salts according as one, two, or three atoms of hydrogen are replaced by their equivalent of metal. Thus we know three orthophosphates of sodium :—

Trisodium or normal sodium phosphate, $Na_3PO_4 + 2H_2O$.
Hydrogen disodium phosphate, $HNa_2PO_4 + 12H_2O$.
Dihydrogen sodium phosphate, $H_2NaPO_4 + H_2O$.

Of the normal salts those of the alkalis, with the exception of the lithium salt, are easily soluble in water and their solutions have a strong alkaline reaction. The normal orthophosphates which are insoluble in water are easily soluble in dilute acids, by which they are converted into the soluble hydrogen orthophosphates. These latter salts are readily obtained from the normal compounds; even carbon dioxide brings about the change; thus, if this gas be led into a solution of trisodium phosphate the following reaction takes place :—

$$Na_3PO_4 + CO_2 + H_2O = HNa_2PO_4 + HNaCO_3.$$

The hydrogen disodium phosphate which is here formed together with hydrogen sodium carbonate is the common phosphate of soda of the shops. This salt, although according to its constitution it must be considered as an acid salt, inasmuch as it still contains hydrogen replaceable by a metal, has a slightly alkaline reaction to methyl orange and litmus, but is neutral to phenolphthalein and is easily obtained by adding the requisite amount of a solution of soda to phosphoric acid. The hydrogen disodium orthophosphate is converted on heating, with loss of water, into the pyrophosphate.

The dihydrogen orthophosphates of the alkalis are soluble in water, and possess a slight acid reaction both to litmus and phenolphthalein, but are neutral to methyl orange. Dihydrogen potassium phosphate, H_2KPO_4, forms large, well defined crystals, and this salt may be heated to a temperature of 400° without losing water. At a higher temperature, however, one molecule of water is driven off and potassium metaphosphate, KPO_3, is formed.

The orthophosphates can readily be recognised by the following reactions. The normal as well as the acid salts give with silver nitrate a yellow precipitate of silver orthophosphate, Ag_3PO_4 :—

$$Na_3PO_4 + 3AgNO_3 = 3NaNO_3 + Ag_3PO_4.$$
$$HNa_2PO_4 + 3AgNO_3 = 2NaNO_3 + HNO_3 + Ag_3PO_4.$$
$$H_2NaPO_4 + 3AgNO_3 = NaNO_3 + 2HNO_3 + Ag_3PO_4.$$

In the case of common sodium phosphate and silver nitrate, we have the singular fact of a neutral and a slightly alkaline solution when mixed, yielding a strongly acid liquid. The reaction which here occurs is somewhat complicated, and the final condition is not correctly represented by the equation given. A certain amount of nitric acid is produced, and equilibrium is then established between the two acids, nitric and phosphoric, and the two bases, soda and silver oxide, which are present, only about 60 per cent. of the total phosphoric acid being precipitated as silver phosphate. The precipitation is never complete unless 1 molecule of caustic soda be added.

A similar reaction occurs with dihydrogen sodium phosphate, but in this case 2 molecules of an alkali must be added to ensure complete precipitation.[1]

When to a solution of an ortho-salt a mixture of sal-ammoniac, ammonia, and magnesium sulphate solutions is added, a crystalline precipitate of ammonium magnesium phosphate,

$$(NH_4)MgPO_4 + 6H_2O,$$

is thrown down. In order to detect orthophosphoric acid in a substance insoluble in water, the body may be dissolved in nitric acid and an excess of a solution of ammonium molybdate in nitric acid added to the liquid. If phosphoric acid be present, this solution on slightly warming, or on standing in the cold, yields a dense yellow precipitate. The composition of this precipitate varies with the conditions of the experiment, but is approximately represented by the following formula :—

$$14MoO_3 + (NH_4)_3PO_4 + 4H_2O.$$

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[1] **Ostwald**, *Wissenschaftliche Grundlagen der analytischen Chemie* (Leipzig, **1904**): **Berthelot**, *Compt. Rend.* 1901, **132**, 1449.

METAPHOSPHORIC ACID, HPO_3.

378 This modification of phosphoric acid was discovered by Graham in 1833. It is obtained when a solution of phosphoric acid is heated until the residue does not give off any more water. The acid thus prepared solidifies on cooling to a soft pasty mass, which, on exposure to the air, readily absorbs moisture and deliquesces. The glacial phosphoric acid of the shops is metaphosphoric acid, which usually contains soda as impurity.[1] Metaphosphoric acid is also formed when crystalline phosphorous acid is heated in a sealed tube with bromine (Gustavson); thus:—

$$H_3PO_3 + Br_2 = HPO_3 + 2HBr.$$

When phosphorus pentoxide is allowed to deliquesce in moist air or when it is dissolved in cold water metaphosphoric acid is formed. This aqueous solution on standing, at the ordinary temperature of the air, gradually undergoes change with formation of common phosphoric acid and this conversion takes place quickly without the formation of the intermediate pyrophosphoric acid if the liquid be boiled (Graham).[2] Metaphosphoric acid is volatile at a bright red heat, and when heated with sulphates expels sulphuric acid from them, for although sulphuric acid is a stronger acid than phosphoric acid, the former is more easily volatile than the latter. An aqueous solution of metaphosphoric acid is also obtained by passing a current of sulphuretted hydrogen gas through a liquid containing lead metaphosphate in suspension.

The solution of metaphosphoric acid is distinguished from those of the other two modifications inasmuch as it produces a white precipitate with solutions of calcium chloride, barium chloride, and albumen.

379 *The Metaphosphates.*—The salts of metaphosphoric acid are obtained by neutralising the aqueous solution of the acid by a base or by heating a dihydrogen orthophosphate; thus:—

$$KH_2PO_4 = KPO_3 + H_2O.$$

No less than five distinct modifications of the metaphosphates are known to exist.[3]

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[1] Brescius, *Zeit. anal. Chem.* 1867, **6**, 187.

[2] See also Berthelot and André, *Compt. Rend.* 1897, **124**, 265; Montemartini and Egidi, *Gazetta*, 1901, **31**, i, 394.

[3] Maddrell, *Mem. Chem. Soc.* **3**, 373.

(1) *Monometaphosphates.*—Of this class only those of the alkali metals are known, such as KPO_3. The monometaphosphates are remarkable as being insoluble in water. The potassium salt is formed, as previously stated, when dihydrogen potassium phosphate is heated. The monometaphosphates are distinguished from the other modifications inasmuch as they do not form any double salts.

(2) *Dimetaphosphates.*—These salts are formed when aqueous phosphoric acid is heated to a temperature of 350° (Fleitmann) or 316° (Maddrell) with the oxides of zinc, manganese, or copper. If the copper salt be then decomposed by potassium sulphide a soluble potassium dimetaphosphate, $K_2P_2O_6$, is obtained and if sodium sulphide be employed a soluble sodium dimetaphosphate is in like manner produced. In addition to the dimetaphosphates containing only one metal, double salts such as $CuK_2(P_2O_6)_2$ can be prepared. Only the dimetaphosphates of the alkali metals are soluble in water and are crystallisable; the others are insoluble or only very slightly soluble (Fleitmann).

(3) *Trimetaphosphates.*—The sodium salt, $Na_3P_3O_9$, is obtained together with the monometaphosphate when microcosmic salt, $(NH_4)HNaPO_4$, is gently heated until the fused mass becomes crystalline (Lindbom). By double decomposition other trimetaphosphates can be obtained from this salt. These are all soluble in water, including the silver salt, and they form double salts such as $NaBaP_3O_9$. The silver salt may be obtained in the form of large transparent monoclinic crystals by allowing a mixture of the sodium salt and silver nitrate solution to stand for some days. In the same way the crystalline lead salt may be prepared by the substitution of nitrate (but not of acetate) of lead for the silver salt.

(4) *Tetrametaphosphates.*—The lead salt, $Pb_2P_4O_{12}$, is formed by treating oxide of lead with an excess of phosphoric acid and heating up to a temperature of 300°. If this is then decomposed by sodium sulphide the sodium salt is obtained as a tetrametaphosphate. This, however, is not a crystalline salt, but forms with a small quantity of water a viscid elastic mass and on the addition of a larger quantity of water a gum-like solution which will not pass through a filter. The tetrametaphosphates of the alkalis produce viscid precipitates with the soluble salts of the alkaline earths. If sodium dimetaphosphate is fused with copper dimetaphosphate and the mixture allowed gradually to cool, a double compound

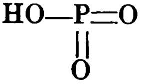
having the composition $CuNa_2P_4O_{12}$ is formed (Fleitmann and Henneberg).

(5) *Hexametaphosphates.*—The sodium salt, $Na_6P_6O_{18}$, is obtained when fused sodium metaphosphate is allowed to cool slowly. It is a crystalline mass, deliquesces on exposure to the air, and produces with barium chloride a flocculent precipitate, and with the salts of the heavy metals gelatinous precipitates.

It also forms characteristic double salts in which five equivalents of the monad metal are replaced by the corresponding amount of a dyad metal, the calcium salt, for example, having the composition $Ca''_5Na_2(PO_3)_{12}$ or $(NaPO_3)_2(Ca''P_2O_6)_5$.

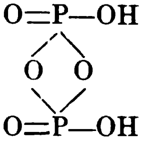
The metaphosphates which are soluble in water have a neutral or slightly acid reaction. When their solutions are boiled they are, as a rule, converted into orthophosphates. All the metaphosphates undergo this change on boiling with nitric acid or when they are fused with an alkali.

The different varieties of metaphosphates are derived from acids, all of which possess the same composition, but differ, as the double salts show, from one another in molecular weight. Compounds of this description are termed *polymeric*. If we assume the constitutional formula now usually accepted for metaphosphoric acid, namely



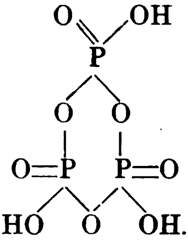
$$\begin{array}{l} HO—\underset{\| \atop O}{P}=O \end{array}$$

the constitution of these hypothetical acids may be represented graphically as follows.—



Dimetaphosphoric Acid.

and



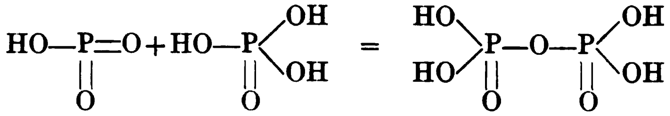
Trimetaphosphoric Acid.

PYROPHOSPHORIC ACID, $H_4P_2O_7$.

380 Common sodium phosphate, or hydrogen disodium phosphate, HNa_2PO_4, when heated to a temperature of 240° loses water, and is converted into sodium pyrophosphate (Graham):

$$2HNa_2PO_4 = H_2O + Na_4P_2O_7.$$

The salt thus obtained dissolves in water, but does not again form an orthophosphate, and is distinguished from the original salt inasmuch as its solutions yield on the addition of silver nitrate a white, and not a yellow, precipitate. This fact was first observed by Clark, of Aberdeen, in the year 1828.[1] It is, however, to Graham that we are indebted for a knowledge of the fact that the heated sodium salt and the silver salt obtained from it are derived from an acid having the composition $H_4P_2O_7$, and that this can be obtained from orthophosphoric acid by heating it for a considerable length of time to a temperature of about 215°. Pyrophosphoric acid is also formed when equal molecules of ortho- and metaphosphoric acids are heated together at 100°.[2]



Pyrophosphoric acid usually forms either a soft glassy mass (Graham) or an opaque indistinctly crystalline mass (Peligot), but slowly crystallises from the syrupy acid at $-10°$ in needles, melting at 61°[3]

An aqueous solution of pyrophosphoric acid is obtained by precipitating the sodium salt with a solution of lead acetate and decomposing the well-washed lead pyrophosphate with sulphuretted hydrogen. The acid solution slowly changes at the ordinary temperature,[4] and when heated is rapidly converted into orthophosphoric acid.

Pyrophosphoric acid may be distinguished from the ortho-modification inasmuch as its solution produces a white granular precipitate with silver nitrate, and from the meta-variety inasmuch as it does not produce a precipitate either with a solution of barium chloride or with one of albumen.

381 *Pyrophosphates.*—These salts are prepared from the mono-hydrogen orthophosphates by heat, or by neutralising a freshly prepared solution of the acid by means of a base. Both normal pyrophosphates, such as $Na_4P_2O_7$, and acid or hydrogen pyrophosphates, such as $H_2Na_2P_2O_7$ exist; the first have an alkaline

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[1] *Edinburgh Journal of Science*, 1828, **7**, 298.

[2] Geuther, *J. pr. Chem.* 1873 [2], **8**, 359.

[3] Giran, *Compt. Rend.* 1902, **135**, 961.

[4] Berthelot and André, *Compt. Rend.* 1896, **123**, 776; Montemartini and Egidi, *Gazzetta*, 1902, **32**, i, 381.

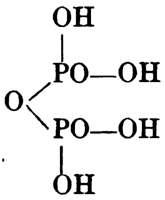
reaction, the second a slightly acid one both to litmus and phenolphthalein, but the acid salt is neutral to methyl orange. The sodium salts, $Na_3HP_2O_7$, and $NaH_3P_2O_7$, are also known.[1] The pyrophosphates of the alkali metals are soluble in water, those of the other metals insoluble, but many of them dissolve in an excess of sodium pyrophosphate. The pyrophosphates in solution remain unaltered in the cold and even on heating do not change, but when boiled with an acid are decomposed, the orthophosphates being formed. The same change takes place on fusion with an alkali.

Tetraphosphates.—A sodium salt having the composition $Na_6P_4O_{13}$, was obtained by Fleitmann and Henneberg by fusing sodium hexametaphosphate with pyrophosphate or orthophosphate, in quantities represented by the following equations:—

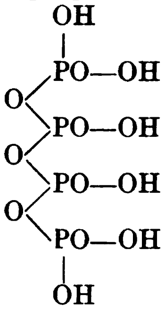
$$Na_6P_6O_{18}+3Na_4P_2O_7=3Na_6P_4O_{13}$$
$$Na_6P_6O_{18}+2Na_3PO_4=2Na_6P_4O_{13}.$$

The salt thus obtained can be crystallised from solution in warm water and gives with silver nitrate a white precipitate, $Ag_6P_4O_{13}$, which does not dissolve in an excess of the sodium salt. The constitution of the pyrophosphates, or the diphosphates as they may be called, and of the tetraphosphates may be exhibited as follows:—

Diphosphoric Acid.



Tetraphosphoric Acid.



382 *Quantitative Estimation of Phosphoric Acid.*—Phosphoric acid is best estimated in the soluble phosphates by adding to the solution a mixture of sal-ammoniac, ammonia, and magnesium sulphate solutions, when a precipitate of ammonium magnesium phosphate occurs, $NH_4MgPO_4+6H_2O$. After this has stood for some time, the solution is filtered off, and the

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[1] Giran, *Compt. Rend.* 1902, **134**, 1499.

precipitate washed with dilute ammonia, dried, converted by ignition into magnesium pyrophosphate, $Mg_2P_2O_7$, and weighed.

The insoluble phosphates must be converted into soluble salts before the determination of the phosphoric acid. If they are soluble in nitric acid, the method proposed by Sonnenschein may be adopted; namely, to precipitate the nitric acid solution of the phosphate by an excess of ammonium molybdate dissolved in nitric acid. On standing for some time at a moderate temperature, a yellow precipitate, containing all the phosphoric acid, is formed; the excess of molybdenum salt is removed by washing with water, the precipitate dissolved in ammonia, and the phosphoric acid precipitated by magnesium sulphate as described above.

If the phosphates will dissolve in acetic acid the phosphoric acid may be precipitated with uranium acetate as uranium phosphate. This method may also be employed for the volumetric determination of phosphoric acid, the point of complete precipitation of the phosphoric acid being ascertained by the addition of a drop of the solution to a drop of a solution of potassium ferrocyanide with which the slightest excess of uranium acetate produces a brown colour.

Metaphosphates and pyrophosphates must first be converted into orthophosphates before precipitation. In like manner phosphorus itself as well as the hypophosphites and phosphites may also be quantitatively determined in the form of phosphoric acid by previously oxidising them with nitric acid.

HALOGEN DERIVATIVES OF PHOSPHORIC ACID.

383 The hydroxyl groups contained in the three modifications of phosphoric acid may be replaced, as is the case with other hydroxyacids, by fluorine, chlorine or bromine, thus giving rise to the oxyfluorides, oxychlorides, and oxybromides of phosphorus, as they are commonly termed.

Phosphorus Oxyfluoride, POF_3, was first obtained by Moissan[1] by exploding a mixture of phosphorus trifluoride and oxygen and is also prepared by heating a mixture of two parts of cryolite and three parts of phosphorus pentoxide in a brass tube,[2] by dropping phosphorus oxychloride on to dried zinc fluoride,[3] or by

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[1] *Compt. Rend.* 1886, **102**, 1245.

[2] Thorpe and Hambly, *Journ. Chem. Soc.* 1889, 759.

[3] *Bull. Soc. Chim.* 1890 [3], **4**, 260,

the action of anhydrous hydrogen fluoride on phosphorus pentoxide.[1] It is a gas which fumes in the air and condenses to a colourless liquid which does not attack glass, boils at −40°, and freezes to a crystalline mass, melting at −68°.[2]

384 *Phosphorus Oxychloride or Phosphoryl Chloride*, $POCl_3$.—This compound was discovered in the year 1847 by Wurtz,[3] who obtained it by decomposing the pentachloride with the requisite quantity of water:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

This substance may be prepared by heating dried oxalic acid with phosphorus pentachloride (Gerhardt[4]), when the following reaction takes place:—

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO.$$

Instead of oxalic acid, boric acid may be employed, thus:—

$$3PCl_5 + 2B(OH)_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

Pure phosphorus oxychloride may also be easily obtained by heating the pentachloride and the pentoxide together in sealed tubes in the proportion of six molecules of the former to one molecule of the latter:[5]

$$6PCl_5 + P_4O_{10} = 10POCl_3.$$

The same compound is also obtained by distilling phosphorus pentoxide with common salt:[6]

$$P_4O_{10} + 3NaCl = POCl_3 + 3NaPO_3.$$

It may conveniently be prepared by gradually adding powdered dry potassium chlorate (32 grams.) to phosphorus trichloride (100 grams.) at the ordinary temperature and then distilling.[7]

Phosphorus oxychloride is also formed as a product of decomposition in the preparation of many acid chlorides. Several examples of this mode of formation have already been mentioned and many more will have to be described.

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[1] *Bull. Soc. Chim.* 1891 [3], **5**, 458.

[2] Moissan, *Compt. Rend.* 1904, **138**, 789.

[3] *Ann. Chim. Phys.* 1847 [3], **20**, 472.

[4] *Ann. Chim. Phys.* 1855 [3], **44**, 102.

[5] Gerhardt and Chiozza, *Annalen*, 1853, **87**, 290.

[6] Kolbe and Lautemann, *Annalen*, 1860, **113**, 240.

[7] Dervin, *Compt. Rend.* 1883, **97**, 576. See also Ullmann and Fornaro, *Ber.* 1901, **34**, 2172.

Phosphorus oxychloride is a colourless mobile liquid boiling at 107°·2 and having a specific gravity of 1·7118 at 0° (Thorpe). When strongly cooled it solidifies in the form of tabular or needle-shaped crystals which melt at −1°·5 (Geuther and Michaelis). It fumes strongly in the air and has a very penetrating and acrid smell resembling that of phosphorus trichloride. According to Cahours the specific gravity of the vapour is 5·334. The oxychloride when thrown into water sinks, and slowly dissolves with the formation of phosphoric and hydrochloric acids:—

$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl.$$

When brought in contact with many metallic chlorides it forms crystalline double compounds.

385 *Pyrophosphoryl Chloride*, $P_2O_3Cl_4$.—When the four hydroxyl-groups in pyrophosphoric acid, $H_4P_2O_7$, are replaced by chlorine, pyrophosphoryl chloride is formed. It was first prepared by Geuther and Michaelis,[1] by the action of nitrogen peroxide on phosphorus trichloride. The reaction which takes place in this case is a somewhat complicated one, nitrogen, nitrosyl chloride, phosphoryl chloride, and phosphorus pentoxide being formed.

It is formed in small amount by the addition of three molecular proportions of water to two of phosphorus pentachloride and by the action of moist air on phosphoryl chloride, and may be prepared by treating six molecular proportions of the pentachloride with one of the pentoxide (P_4O_{10}).[2]

Pyrophosphoryl chloride is a colourless strongly fuming liquid boiling between 210° and 215° and then undergoing partial decomposition into pentoxide and common oxychloride, metaphosphoryl chloride being formed as an intermediate product:—

$$6P_2O_3Cl_4 = P_4O_{10} + 8POCl_3.$$

At 7° the specific gravity of the liquid is 1·78; it decomposes violently in contact with water without sinking in it, and in this decomposition orthophosphoric acid and not pyrophosphoric acid is formed. When it is treated with pentachloride of phosphorus, phosphoryl chloride is produced:—

$$P_2O_3Cl_4 + PCl_5 = 3POCl_3.$$

By the action of phosphorus pentoxide on phosphorus oxy-

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[1] *Ber.* 1871, **4**, 766.

[2] Oddo, *Gazzetta*, 1899, **29**, ii, 330.

chloride, Gustavson[1] obtained a syrupy mass which he regarded as *metaphosphoryl chloride*, PO_2Cl. Hambly[2] has, however, shown that this is a mixture of at least two compounds, one of which is pyrophosphoryl chloride; the other constituent has a constant composition, but cannot from the analysis have a simpler formula than $P_7O_{15}Cl_5$ and is probably itself a mixture.

Metaphosphoryl chloride is, however, formed by the action of a small amount of water on phosphoryl chloride.[3]

Phosphorus Oxybromide, or Phosphoryl Bromide, $POBr_3$.—This body is formed by the action of a small quantity of water upon the pentabromide, but it is best prepared by distilling pentabromide of phosphorus with oxalic acid (Baudrimont). It forms a mass of flat tabular crystals which have a specific gravity of 2·822 (Ritter), melt at 46° and boil at 195°. Water decomposes the oxybromide into phosphoric and hydrobromic acids.

Phosphoryl Bromodichloride, $POBrCl_2$.—When phosphorus trichloride is allowed to fall drop by drop into absolute alcohol, $C_2H_5(OH)$, the first action that takes place is the formation of the compound $(C_2H_5O)PCl_2$. This body is decomposed by the addition of bromine into ethyl bromide, C_2H_5Br, and phosphorus oxybromodichloride, $POBrCl_2$. This latter compound is a highly refractive liquid, boiling at 136° and having at 0° a specific gravity of 2·049 (Menschutkin). When the liquid is cooled it solidifies in the form of tabular crystals melting at 13°, and probably isomorphous with the crystals of phosphoryl chloride and phosphoryl bromide (Geuther and Michaelis). It is also produced by the action of hydrogen bromide on the vapour of phosphoryl chloride at 400–500°, and is then accompanied by *phosphoryl dibromochloride*, $POBr_2Cl$, which melts at 30° and boils at 165°.[4]

PHOSPHORUS AND SULPHUR.

386 The compounds formed by these two elements were formerly divided into two classes according as they contained a greater number of atoms of phosphorus or sulphur. Two compounds of the former class have been described, namely, sulphur

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[1] *Ber.* 1871, **4**, 853.

[2] *Journ. Chem. Soc.* 1891, 202.

[3] Besson, *Compt. Rend.* 1897, **124**, 1099.

[4] Besson, *Compt. Rend.* 1896, **122**, 814.

tetraphosphide SP_4 and sulphur diphosphide SP_2, but later researches[1] have shown that these substances are in reality simply solutions of sulphur in phosphorus, for no heat is evolved in their formation from the elements, and a current of an indifferent gas removes the whole of the phosphorus at temperatures below its boiling point.

The sulphides of phosphorus are solid bodies formed when phosphorus and sulphur are gently heated together, the reaction being accompanied by the evolution of heat. If common phosphorus is employed for this purpose violent explosions may occur, and hence it is advisable to employ red phosphorus. Even in the latter case, when finely divided sulphur such as flowers of sulphur, is employed, the reaction is often very violent, and for this reason the sulphides of phosphorus are best prepared by mixing the necessary quantity of red phosphorus with small lumps of roll sulphur. The mixture is effected in a flask, the cork loosely placed in, and the flask then heated on a sand bath by means of a Bunsen flame, until the reaction begins, when the flame is removed. After the flask has cooled it may be broken to obtain the solid mass which is then preserved in dry well-closed bottles (Kekulé).

There appears to be no doubt that the sulphides P_4S_3, P_3S_6, and P_2S_5, can be prepared in this way, but the individuality of several other sulphides which have been described cannot yet be considered as definitely established. Such are the sulphides P_4S_6 (Isambert[2]) and P_4S_7 (Helff), obtained by the foregoing method, as well as the compounds P_3S_5 and P_8S_{11}, prepared by heating the sulphide P_4S_3 with sulphur in presence of carbon bisulphide (Dervin,[3] Boulouch[4]).

Tetraphosphorus Trisulphide (*Phosphorus Sesquisulphide*), P_4S_3. —This compound is obtained as a yellow mass, crystallising from solution in carbon bisulphide or phosphorus trichloride in the form of rhombic prisms. It melts at 166° (Ramme), forming a reddish liquid, which boils about 380° (Isambert). When heated in a current of carbon dioxide it sublimes at 260° and condenses to form crystals, which appear to belong to the regular system. The specific gravity of its vapour is 7·90. It is very easily inflammable and is slowly decomposed in contact with

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[1] Schultze, *J. pr. Chem.* 1880 [2], **22**, 113; *Ber.* 1883, **16**, 2066; Isambert, *Compt. Rend.* 1883, **96**, 1499, 1628, 1721; Helff, *Zeit. physikal. Chem.* 1893, **12**, 196; Boulouch, *Compt. Rend.* 1902, **135**, 165.

[2] *Compt. Rend.* 1886, **102**, 1386. [3] *Ibid.* 1904, **138**, 365. [4] *Ibid.* 363.

boiling water with formation of sulphuretted hydrogen, phosphine and phosphorous acid:—

$$P_4S_3 + 9H_2O = 3SH_2 + 3P(OH)_3 + PH_3.$$

This substance is now largely used as a substitute for white phosphorus in the heads of matches. When pure it does not give Mitscherlich's phosphorescence test for free phosphorus (p. 611), but on exposure to moist air partial oxidation occurs and a decided reaction is then given.[1]

Triphosphorus Hexasulphide, P_3S_6.—This is obtained in crystalline needles, melting from 296°—298°, by heating yellow phosphorus and sulphur with carbon bisulphide for some hours to 210°, and is also formed when a solution of sulphur and the sulphide P_4S_3 in carbon bisulphide, or one of phosphorus and sulphur in the same solvent in presence of a crystal of iodine, is exposed to light. (Dervin, Boulouch.) The above molecular formula was established by a vapour density determination (Ramme).[2]

Phosphorus Pentasulphide, P_2S_5.—In order to prepare this compound in the pure state, the crude sulphide prepared by Kekulé's method is distilled in a current of carbon dioxide. A pale yellow crystalline mass is thus obtained and frequently distinct crystals.[3] When a mixture of yellow phosphorus and sulphur in the proper proportions is heated with carbon bisulphide to 210°, fine, pale yellow crystals separate out (Ramme). Phosphorus pentasulphide melts at 274°—276°, boils at 518° (Goldschmidt), and yields a brown vapour having a specific gravity of 7·67 (C. and V. Meyer). Water decomposes this substance as follows:—

$$P_2S_5 + 8H_2O = 2PO(OH)_3 + 5H_2S.$$

Phosphorus pentasulphide is often used in making organic preparations for the purpose of replacing oxygen in organic compounds by sulphur. Thus, for instance, if common alcohol, $C_2H_5.OH$, be heated with this body, thioalcohol or mercaptan, $C_2H_5.SH$, is formed.

387 *Phosphorus Sulphoxide*, $P_4O_6S_4$, is obtained by carefully heating phosphorous oxide with the calculated quantity of sulphur to 150°—170°, the product when heated *in vacuo* subliming in

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[1] Clayton, *Proc. Chem. Soc.* 1902, 129; 1903, 231; Mai and Scheffer, *Ber.* 1903, **36**, 870.

[2] *Ber.* 1879, **12**, 940, 1350.

[3] Carl Meyer and V. Meyer, *Ber.* 1879, **12**, 610.

colourless strongly refractive crystals. It melts at about 102°, and boils at 295°, yielding a vapour whose density corresponds to the formula, $P_4O_6S_4$. It rapidly deliquesces in the air and is quickly dissolved by water, forming sulphuretted hydrogen and metaphosphoric acid, which is eventually converted into orthophosphoric acid:—

$$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S.$$

A *sulphoxide*, $P_2O_2S_3$, is also produced by the action of sulphuretted hydrogen on phosphoryl chloride at 0°. It forms acicular crystals, and decomposes at 200° into the pentoxide and pentasulphide.[1]

MONOTHIOPHOSPHORIC ACID, H_3PSO_3.

This substance may be regarded as phosphoric acid in which one atom of sulphur replaces one atom of oxygen. It is, however, not known in the free state. The sodium salt, Na_3PSO_3, is produced when the chloride (described below) is heated with caustic soda. The salt forms distinct crystals, which have an alkaline reaction, and it is decomposed by the weakest acids, the thiophosphoric acid which is thus liberated being at once decomposed into sulphuretted hydrogen and phosphoric acid; thus:—

$$PS(OH)_3 + H_2O = PO(OH)_3 + SH_2.$$

Dithiophosphoric acid, $H_3PS_2O_2$, and trithiophosphoric acid, H_3PS_3O, are also known in their salts.[2]

Several series of thiophosphates may be prepared by heating various metals with phosphorus and sulphur.[3]

THIOPHOSPHORYL DERIVATIVES.

388 *Thiophosphoryl fluoride*, PSF_3, is obtained by the action of thiophosphoryl chloride on arsenic fluoride, but is best prepared by heating a mixture of carefully dried lead fluoride and phosphorus pentasulphide to 170°—250°, the following reaction taking place:—

$$P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3.$$

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[1] Besson, *Compt. Rend.* 1897, **124**, 151.

[2] Kubierschky, *J. pr. Chem.* 1885 [2], **31**, 93.

[3] Ferrand, *Bull. Soc. Chem.* 1895 [3], **13**, 115; *Compt. Rend.* 1896 **122**, 886.

At the ordinary temperature it is a transparent colourless gas, which condenses to a liquid under a pressure of 10—11 atmospheres. It does not attack dry glass, but is spontaneously inflammable in air or oxygen, and is decomposed by heat or the electric spark with separation of sulphur and phosphorus and formation of phosphorus fluorides. The products obtained by the action of oxygen consist of phosphorus pentafluoride, phosphorus pentoxide and sulphur dioxide, whilst with water it yields sulphuretted hydrogen, phosphoric and hydrofluoric acids.[1]

Thiophosphoryl Chloride, $PSCl_3$, which corresponds to phosphorus oxychloride, is best obtained by acting upon phosphorus pentachloride with phosphorus pentasulphide (Weber):

$$3PCl_5 + P_2S_5 = 5PSCl_3.$$

It is a colourless, mobile, very refractive liquid, which fumes strongly in the air, possesses a powerful pungent odour, freezes at $-35°$, boils at 125°, and has a specific gravity at 0° of 1·16816 (Thorpe). The specific gravity of the vapour, according to Cahours, is 5·878 at 298°. It is decomposed by water into hydrochloric acid and thiophosphoric acid, which is then further decomposed as described above.

Thiosphosphoryl Bromide, $PSBr_3$.—According to Baudrimont this body is obtained by distilling phosphorus tribromide with flowers of sulphur. It is, however, best prepared by dissolving equal parts of sulphur and phosphorus in carbon bisulphide, and adding gradually to the well-cooled liquid eight parts of bromine. On distillation the carbon bisulphide first comes over and then the thio-bromide. This is purified by shaking it up several times with cold water; a hydrate is formed in this way having the composition $PSBr_3 + H_2O$, which on being warmed to 35° separates into its constituents. The anhydrous compound is obtained by the evaporation of the solution in carbon bisulphide as a yellow liquid, which, when touched by a solid body, at once solidifies to a crystalline mass. This compound can also be obtained in the crystalline state from solution in phosphorus tribromide, when it separates out in regular octahedra, having a yellow colour and melting at 38°. When heated with water it is slowly decomposed and on distillation is resolved partly into sulphur and into a compound, $PSBr_3PBr_3$, which boils at 205°.[2]

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[1] Thorpe and Rodger, *Journ. Chem. Soc.* 1889, 306.

[2] Michaelis, *Annalen*, 1857, **104**, 9.

Thiophosphoryl chloride is decomposed by hydrogen bromide at 400°—500°, forming the bromide and two chlorobromides; *thiophosphorylbromodichloride*, $PSCl_2Br$, which boils at 108° under 6 mm. pressure and freezes at $-30°$; and *thiophosphoryl dibromochloride*. $PSClBr_2$, which melts at $-6°$ and boils at 95° under 6 mm. pressure.[1]

389 *Thiopyrophosphoryl bromide*, $P_2S_3Br_4$.—This compound, the sulphur analogue of pyrophosphoryl chloride, is obtained by pouring carbon bisulphide over phosphorus trisulphide and adding to it, drop by drop, a solution of bromine in carbon bisulphide.[2] It forms a light yellow oily liquid which fumes in the air, has an aromatic and pungent smell, and on heating decomposes into the ortho-compound and phosphorus pentasulphide; thus:—

$$3P_2S_3Br_4 = 4PSBr_3 + P_2S_5.$$

Phosphorus thioiodide, P_2SI_2, is formed[3] as an orange coloured solid, melting at about 75°, when thiophosphoryl chloride is treated with hydrogen iodide at about 30°. A second *thioiodide*, P_2S_3I, has been obtained by the direct union of its elements in presence of carbon bisulphide at 120°, and crystallises in golden yellow prisms.[4]

PHOSPHORUS AND SELENIUM.

390 Phosphorus and selenium can be fused together in all proportions forming a red mass, but it seems probable that only the definite compounds of the formulæ, P_4Se_3,P_2Se_5, and perhaps P_2Se_3, exist. These substances are decomposed by moist air, and when treated with alkalis or alkali sulphides yield complex salts, such as potassium thioselenophosphite, $2K_2S,P_2Se_3,5H_2O$.[5]

PHOSPHORUS AND NITROGEN.

391 A very stable compound of phosphorus and nitrogen is known, and a number of derivatives of phosphorous and phosphoric acids containing this element have also been prepared.

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[1] Besson, *Compt. Rend.* 1896, **122**, 1057.

[2] Michaelis, *Annalen*, 1857, **104**, 9.

[3] Besson, *Compt. Rend.* 1896, **122**, 1200.

[4] Ouvrard, *Compt. Rend.* 1892, **115**, 1301.

[5] Muthmann and Clever, *Zeit. anorg Chem.* 1896, **13**, 191; Meyer, *Zeit. anorg. Chem.* 1902, **30**, 258.

Phosphorus nitride, P_3N_5.—Phosphorus pentasulphide readily unites with six and with seven molecules of ammonia, and when either of these compounds is heated to 230° in ammonia and then at a higher temperature in a current of hydrogen, decomposition occurs, and at a bright red heat phosphorus nitride is left behind. This is a white, odourless amorphous substance, and decomposes into phosphorus and nitrogen when heated above bright redness for some time. It is scarcely affected by boiling water, but is completely decomposed by water at 180°, ammonia and phosphoric acid being formed. It takes fire when heated in chlorine or oxygen, and is decomposed by many metals.[1]

Phosphorous diamide, $HO.P(NH_2)_2$, is obtained by the action of ammonia on a solution of phosphorous oxide in ether or benzene. It is a white powder which dissolves in water instantly, with such violence that it becomes incandescent. When treated with moderately dilute hydrochloric acid, a violent reaction occurs, with liberation of non-spontaneously inflammable phosphine, separation of free phosphorus, and formation of a solution of ammonium chloride, phosphorous and phosphoric acids.[2]

Amidophosphoric acid or Phosphamidic acid, $NH_2.PO(OH)_2$. —The potassium salt of this acid is obtained by the action of potash on the corresponding phenyl salt. The free acid, which is prepared by decomposing the silver salt with sulphuretted hydrogen and adding alcohol to the filtered solution, crystallises in colourless microscopic crystals, which have a sweet taste, and are not hydrolysed by caustic alkalis. It forms both normal and acid salts.[3]

Diamidophosphoric acid, $(NH_2)_2PO.OH$, is obtained in a similar manner to the foregoing compound.[4] It is a crystalline substance and is converted by nitrous acid, first into monamidophosphoric acid and then into orthophosphoric acid. In addition to the normal silver salt, $(NH_2)_2PO.OAg$, it forms a remarkable compound of the formula $(NHAg)_2P(OAg)_3$, derived from the unknown acid $(NH_2)_2P(OH)_3$.

392 When dry ammonia is passed over phosphorus pentachloride as long as it is absorbed, a white mass is obtained, consisting probably of a mixture of the compound $PCl_3(NH_2)_2$

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[1] Stock and Hofmann, *Ber.* 1903, **36**, 314.

[2] Thorpe and Tutton, *Journ. Chem. Soc.* 1891, 1027.

[3] H. N. Stokes, *Amer. Chem. J.* 1893, **15**, 198.

[4] H. N. Stokes, *Ber.* 1894, **27**, 565.

and NH_4Cl. No method of separating these is known, but if the product be treated with water ammonium chloride dissolves, and the chloramido-compound is decomposed with loss of hydrochloric acid, and is converted into *phosphamide* $PO(NH)NH_2$. This remains behind as a white insoluble powder, which is slowly converted by the boiling liquid into acid ammonium phosphate :—

$$PO(NH)NH_2 + 3H_2O = PO(OH)(ONH_4)_2.$$

Phospham, PHN_2.—If the product of the reaction of ammonia and phosphorus pentachloride is heated in absence of air until no further fumes of ammonium chloride are evolved, a light white powder having the above composition remains behind, to which the name phospham has been given.[1] It is insoluble in water and does not melt at a red heat, but oxidises on heating in the air, with evolution of white fumes. If it be moistened with water and then heated, metaphosphoric acid and ammonia are formed :—

$$3PHN_2 + 9H_2O = 3PO_3H + 6NH_3.$$

When fused with potash it decomposes with evolution of light and heat :—

$$3PHN_2 + 9KOH + 3H_2O = 3PO(OK)_3 + 6NH_3.$$

Its exact molecular weight has not yet been ascertained.

Phosphoryl nitride, PON, is obtained by heating phosphamide to redness in absence of air, or by subjecting the product of the reaction of ammonia and phosphorus oxychloride at 0° to the same treatment. It forms a white amorphous powder, which melts at a red heat, and resolidifies to a glassy mass. It is not acted upon by nitric acid, but when fused with caustic alkalis is converted into ammonia and potassium orthophosphate,

$$PON + 3KOH = PO(OK)_3 + NH_3.$$

THE PHOSPHONITRILE CHLORIDES AND THE METAPHOSPHIMIC ACIDS.

393 A substance of the composition $PNCl_2$ was first obtained by Liebig and Wöhler among the products of the reaction of ammonia and phosphorus pentachloride, and has been more

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[1] Liebig and Wöhler, *Annalen*, 1834, **11**, 146; Hofmann, *Ber* 1884, **17**, 1909; Besson, *Compt. Rend.* 1892, **114**, 1264.

closely investigated by Gladstone,[1] Wichelhaus,[2] Besson,[3] and H. N. Stokes.[4]

When molecular proportions of phosphorus pentachloride and ammonium chloride are heated together in a sealed tube, a complicated mixture of substances is formed, all of which have the empirical formula $PNCl_2$, and may be termed phosphonitrile chlorides. By processes of fractional distillation and recrystallisation from benzene no fewer than six compounds have been isolated, the properties of which are summarised below. All these substances are converted by heat into the last member of the series, polyphosphonitrile chloride, which resembles indiarubber in its appearance and breaks down or depolymerises when heated, yielding the lower members of the series.

Name and Molecular Formula.	Melting Point.	Boiling Point.	
		13 mm.	760 mm.
Triphosphonitrile chloride . . $(PNCl_2)_3$	114°	127°	256·5°
Tetraphosphonitrile chloride $(PNCl_2)_4$	123·5°	188°	328·5°
Pentaphosphonitrile chloride $(PNCl_2)_5$	40·5–41°	223–224·3°	polymerises
Hexphosphonitrile chloride. $(PNCl_2)_6$	91°	261–263°	,,
Heptaphosphonitrile chloride $(PNCl_2)_7$	liquid at − 18°	289–294°	,,
Polyphosphonitrile chloride $(PNCl_2)_x$	below red heat	—	—

These chlorides are all slowly decomposed by water with the production of the corresponding metaphosphimic acids $(PNO_2H_2)_n$. Thus the trichloride yields the hexabasic *trimetaphosphimic acid*, $P_3N_3O_6H_6$, which is readily soluble and yields crystalline salts. The octobasic *tetrametaphosphimic acid*, $P_4N_4O_8H_8 + 2H_2O$, is the best defined and most stable acid of the series; it crystallises well, yields crystalline salts, and is not affected by boiling aqua regia. The penta- and hex-acids have the normal composition but yield amorphous salts, and the heptachloride yields an acid $(PNO_2H_2)_7 + H_2O$. These acids probably contain a ring or closed chain composed of nitrogen and phosphorus atoms; thus the tetra-acid may be

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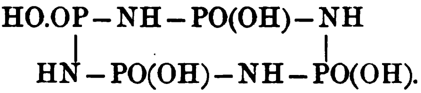
[1] *Journ. Chem. Soc.* 1869, 15.

[2] *Ber.* 1870, **3**, 163.

[3] *Compt. rend.* 1892, **114**, 1264, 1479.

[4] *Ber.* 1895, **28**, 437. *Amer. Chem. J.* 1896, **18**, 629, 780; 1897 **19**, 782; 1898, **20**, 740.

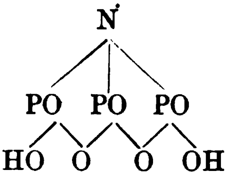
represented by the formula



$$\begin{array}{l} \mathrm{HO.OP-NH-PO(OH)-NH} \\ \quad | \qquad\qquad\qquad\qquad\qquad | \\ \mathrm{HN-PO(OH)-NH-PO(OH).} \end{array}$$

Many salts and decomposition products of these acids have also been examined (H. N. Stokes).

In addition to these Mente, has also prepared *nitrilotrimetaphosphoric acid*, which has the constitution:—

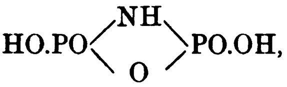


Phosphoryl triamide, $PO(NH_2)_3$, has been described by Schiff, but later investigators have failed to obtain it, his compound being probably impure diimidodiphosphamic acid (see below).

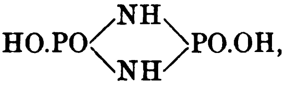
394 *Imidodiphosphoric Acids.*—The action of ammonia on phosphorus oxychloride was investigated many years ago by Gladstone[1] and by Schiff.[2] The former succeeded in obtaining from the product a number of acids, which he regarded as pyrophosphamic acids, or acids derived from pyrophosphoric acid by the replacement of hydroxyl by the group NH_2. The later investigations of Mente[3] have, however, shown that these acids are in reality formed from diphosphoric acid by the replacement of one or more oxygen atoms by the imido group NH, and they may therefore be termed imidodiphosphoric acids.

The constitution of these acids is probably as follows:—

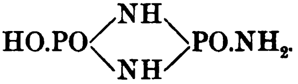
Imidodiphosphoric acid,



Diimidodiphosphoric acid,



Diimidodiphosphamic acid,



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[1] *Annalen*, 1850, **76**, 74. *Journ. Chem. Soc.* 1850, 121; 1851, 135, 353; 1864, 215; 1866, 290; 1868, 64, 261; 1869, 15.

[2] *Annalen*, 1857, **101**, 299; **102**, 113; **103**, 169.

[3] *Annalen*, 1888, **248**, 232.

ARSENIC. $As = 74{\cdot}4\ (H = 1).$
$= 75{\cdot}0\ (O = 16).$

395 The yellow and red sulphides of arsenic, now termed orpiment and realgar, were known to the ancients, although they did not distinguish between them. Aristotle gave to them the name of *σανδαράχη*, which was also applied to cinnabar and red lead, and Theophrastus mentioned them under the name of *ἀρσενικόν*.

White arsenic or arsenious oxide, As_4O_6, is first distinctly mentioned in the writings of the Greek alchemist Olympiodorus, who describes it under the name of white alum, and gives a recipe for its preparation from the sulphide by roasting in the air.[1] The later alchemists were all acquainted with these substances. Thus, for instance, in the works attributed to Basil Valentine, they are described as follows: "In its colour the arsenicum is white, yellow, and red; it is sublimed by itself without any addition, and also with addition according to manifold methods."

The alchemists made use of arsenic especially for the purpose of colouring copper white (see p. 7). The change thus brought about was believed to be the beginning of a transmutation, although Albertus Magnus was aware that on strongly heating the alloy the arsenic is volatilised. He describes this fact in his work *De rebus Metallicis* as follows:—"Arsenicum aeri conjunctum penetrat in ipsum, et convertit in candorem; si tamen diu stet in igne, aes exspirabit arsenicum, et tunc redit pristinus color cupri, sicut de facile probatur in alchymicis."

Free arsenic was known to the Greek alchemists, who obtained it as a sublimate capable of turning copper white, and hence looked upon it as a kind of mercury.[2]

That a metal-like substance is contained in white arsenic was probably known to the Latin Geber, but Albertus Magnus was the first to state this distinctly: "Arsenicum fit metallinum fundendo cum duabus partibus saponis et una arsenici." Metallic arsenic was considered by the later alchemists and chemists to be a bastard or semi-metal, and was frequently termed *arsenicum rex*. It was, however, Brandt who in the year 1773 first showed that white arsenic is a calx of this

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[1] Berthelot, *Introduction à l'Étude*, &c. p. 68.

[2] *Ibid.* p. 99.

substance. After the overthrow of the phlogistic theory the views concerning the composition of white arsenic were those which are now held, namely, that it is an oxide of the elementary substance.

Arsenic occurs in the free state in nature, usually in mammillated or kidney-shaped masses, which readily split up into laminæ. Occasionally, however, native arsenic is met with in distinct crystals. It occurs in large quantity at Andreasberg in the Harz, in Joachimsthal in Bohemia, at Freiberg in Saxony, at Zimeoff in Siberia, in Borneo, and at Newhaven in the United States.

Arsenic occurs much more commonly in a state of combination in many ores and minerals, of which the following are the most important: arsenical iron, $FeAs_2$; tin white cobalt $(CoNiFe)As_2$; arsenical nickel, $NiAs$; arsenical pyrites or mispickel, Fe_2S_2As; realgar, As_2S_2; and orpiment, As_2S_3. Less frequently we find white arsenic or arsenious oxide as arsenite, As_4O_6, and several salts of arsenic acid, such as

Pharmacolite, $(HCaAsO_4)_2 + 5H_2O$,
Cobalt bloom, $Co_3(AsO_4)_2 + 8H_2O$,
Mimetesite, $2Pb_3(AsO_4)_2 + Pb_2(PO_4)Cl$.

Small quantities of arsenic also occur in many other minerals and in many crystalline rocks.[1] Thus, for instance, it is contained in almost all specimens of iron pyrites, so that it is often found in the sulphuric acid which is manufactured from pyrites, and in the many preparations for which this acid serves.

It also occurs in many coals, and thence passes into the air with the smoke, so that dust from towns is found to contain arsenic.[2]

Especially remarkable is the occurrence of arsenic in almost all mineral waters, in which it is only contained in traces (Will, Fresenius). Similarly it has been detected in sea-water, whilst traces of arsenic are stated to occur normally in certain organs of the body.[3]

396 *Preparation.*—The arsenic occurring in commerce is either the natural product, which is never quite pure but contains iron and other metals mixed with it, or, more generally, that obtained by heating arsenical pyrites in earthenware tubes in a furnace.

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[1] Gautier, *Compt. Rend.* 1901, **132**, 932.

[2] Delepine, *Journ. San. Inst.* 1902, **23**, iii. 244.

[3] Gautier, *Compt. Rend.* 1903, **137**, 295.

These tubes are 1 metre in length and about 32 cm. wide. In the open end of this earthenware tube another is placed, made of sheet iron, about 20 cm. long, so that half of the iron tube is inside the earthenware one. The arsenic sublimes into the iron tube, from which it is obtained by unrolling the sheet iron. Prepared by this process, arsenic forms a compact, brittle, crystalline mass having a strong metallic lustre. The decomposition which takes place is represented by the equation:—

$$Fe_2S_2As = 2FeS + As.$$

In Silesia it is prepared from arsenious oxide, which is heated with charcoal in an earthen crucible covered with a conical iron cap, into which the arsenic sublimes.

In order to purify the commercial arsenic it is sublimed with the addition of a small quantity of powdered charcoal. On the small scale, arsenic may be purified by introducing the mixture into a glass flask, which is then placed in a large crucible, surrounded by sand, and heated to redness. As soon as the sublimation begins, a loosely-fitting stopper of chalk is placed in the neck of the flask, a second crucible is placed over the first, and the whole heated until the arsenic is sublimed into the upper portion of the flask. In this way rhombohedral crystals of arsenic are obtained, which have a bright metallic lustre and are isomorphous with those of tellurium and antimony (Mitscherlich).

Properties—Arsenic has a steel-grey colour. Its specific gravity at 14° is 5·727, its specific heat 0·083 (Wüllner and Bettendorf), and it is a good conductor of electricity. If pure arsenic is quickly sublimed in a stream of hydrogen gas it is deposited in the neighbourhood of the heated portion of the tube in crystals, but, at a little distance, as a black glittering mass, and, still further on, as a yellow powder. Both the black[1] and the yellow[2] modifications are crystalline, the former having a specific gravity of 4·713 and the latter of 3·70.[3] Yellow arsenic, which was first obtained by Schüller,[4] is best prepared by distilling arsenic in a stream of carbon dioxide, the vapours being passed into a U-tube, where the arsenic is condensed by coming into contact with another stream of carbon dioxide

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[1] Retgers, *Zeit. anorg. Chem.* 1893, **4**, 403; 1894, **6**, 317.

[2] Linck, *Ber.* 1899, **32**, 881.

[3] Geuther, *Annalen*, 1887, **240**, 208.

[4] *Math. u. naturw. Ber. aus Ungarn*, 1889, **6**, 94.

which has been cooled; the arsenic is then dissolved in carbon bisulphide, from which it is deposited by evaporation or by cooling to − 70°.[1]

This form of arsenic is extremely sensitive to light, changing quickly into the ordinary one, but a solution in carbon bisulphide may be kept for some time unchanged, whilst both the yellow and the black modifications give metallic arsenic on heating.

A reddish-brown crystalline modification, which is not changed by light, is stated to be deposited from a solution of the yellow arsenic in carbon bisulphide on long standing.[2]

It was formerly supposed that arsenic could not be melted, for when heated under ordinary circumstances to about 450° it passes at once from the solid to the gaseous state. Landolt[3] has, however, shown that under an increased pressure it melts at 500°. On cooling, the fused mass forms a dense crystalline solid which has, at 19°, a specific gravity of 5·709. Its melting point lies between those of antimony and silver (Mallet).

The vapour of arsenic is of a lemon-yellow colour and smells disagreeably of garlic. It is, however, still uncertain whether this smell is due to the element itself, or to a low oxide which has not yet been isolated. The specific gravity of the vapour at 860° was found by Deville and Troost to be 10·2, whilst Meyer and Biltz[4] obtained the values 5·45 at 1714° and 5·37 at 1736°. The molecule of arsenic at these high temperatures therefore consists of two atoms, whilst at 860° the vapour density points to the presence of four atoms in the molecule. The molecular formula of yellow arsenic in carbon bisulphide solution[5] as ascertained by the boiling point method is As_4.

Arsenic oxidises somewhat rapidly in moist air at the ordinary temperature, becoming covered with a blackish-grey coating. Heated in oxygen it burns with a bright white flame, forming arsenious oxide, which is also produced when arsenic is heated in the air; at the same time the alliaceous smell of its vapour is perceived. In the act of combination with oxygen, 1 gram of arsenic evolves, according to Thomsen, 1031 thermal units, whilst by its combination with chlorine, in which gas finely powdered arsenic takes fire spontaneously, it evolves 953 thermal units. It is easily oxidised by nitric acid, and also by concentrated

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[1] Erdmann and Unruth, *Zeit. anorg. Chem.* 1902, **32**, 437.

[2] *Ibid.* [3] *Jahrbuch f. Min.* 1859, 733. [4] *Ber.* 1889, **22**, 725.

[5] Erdmann and Unruth, *Zeit. anorg. Chem.* 1902, **32**, 437.

sulphuric acid with evolution of sulphur dioxide, whilst it combines with various non-metals, and with most of the metals. It stands in such close proximity to the latter class of elements, especially in its physical properties, such as lustre, specific gravity, &c., that some chemists have placed it amongst them. Metallic arsenic is chiefly used for the purpose of hardening lead in the manufacture of shot.

The atomic weight of arsenic was first determined by Berzelius,[1] who heated 2·203 grm. of As_4O_6 with sulphur, and obtained 1·069 of SO_2, hence As=74·44. By the analysis of the trichloride Dumas[2] obtained As=74·39, whilst Kessler[3] by oxidising As_4O_6 to As_2O_5 found As=74·7. The most accurate value of the atomic weight is probably 74·4.

ARSENIC AND HYDROGEN.

These two elements unite to form a gaseous compound, AsH_3, and a solid compound, As_2H_2.

HYDROGEN ARSENIDE, OR ARSINE, $AsH_3 = 77·4$.

397 The existence of this gas was first noticed by Scheele in 1775 on treating a solution of arsenic acid with zinc. He found that the gas thus evolved deposited white arsenic on burning, and explained this as being due to the fact that the inflammable air had dissolved some arsenic. Proust showed in 1799 that the same gas is given off when arsenious acid and dilute sulphuric acid are brought together in the presence of zinc, and also when sulphuric acid is allowed to act on arsenical metals. The gas which is thus given off is a mixture of hydrogen and arsine.

In order to prepare arsine in the pure state, zinc arsenide, As_2Zn_3, must be decomposed by dilute sulphuric acid,[4]

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$

Zinc arsenide is obtained by heating zinc and arsenic together in a closed crucible, when heat enough is evolved to melt the mass. The greatest care must be taken in the preparation of

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[1] *Pogg. Ann.* 1824, **8**, 1.
[2] *Annalen*, 1860, **113**, 29.
[3] *Pogg. Ann.* 1855, **95**, 204; 1861, **113**, 134.
[4] Soubeiran, *Ann. Chim. Phys.* 1830, **43**, 407.

arsine, as it is extremely poisonous, a quantity no larger than one bubble having been known to produce fatal effects. Gehlen lost his life in this way in the year 1815.

Arseniuretted hydrogen, as the gas was formerly called, is also formed by the electrolysis of arsenious acid (Bloxam), and in small quantity when arsenic is boiled with water.[1]

398 *Properties.*—Arsine has a very peculiar and disagreeable smell, and, according to Dumas, possesses a specific gravity of 2·695. It liquefies at $-40°$ (Stromeyer), but it does not solidify when cooled to a temperature of $-110°$. Arsine is formed from its elements with absorption of heat, and, like many other compounds of the same class, can be made to undergo explosive decomposition into its elements when exposed to the shock produced by the detonation of fulminate of mercury, although it does not explode when heated.[2] It burns with a pale bluish flame, emitting dense clouds of arsenious oxide. If a cold piece of white porcelain be held in the flame, metallic arsenic is deposited as a brown or black shining mirror, and when the gas is passed through a glass tube which is heated by means of a gas flame, the arsenic is deposited near the heated portion of the tube in the form of a bright shining mirror, the hydrogen being liberated. This decomposition takes place at 230°.[3]

Whenever hydrogen is liberated by means of an acid from any liquid containing arsenic in solution, traces of arsine are evolved. This may be easily detected either by the smell or by the above-mentioned reactions, which are of such delicacy that 0·001 mgrm. ($\frac{1}{70000}$ of a grain) can with certainty be recognised.

When arsine is led over heated oxide of copper, water and copper arsenide are formed, and in this way arsine can easily be estimated quantitatively. When metals such as tin, potassium, or sodium are heated in the gas the arsenides of the metals are formed, free hydrogen, which occupies $1\frac{1}{2}$ times the volume of the original arsine, being generated. The arsenides of potassium and sodium, AsK_3 and $AsNa_3$, are decomposed by dilute acids, yielding arsine which is purer than that obtained from zinc arsenide (Janowsky).

Arsine when passed into a dilute solution of a gold or silver

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[1] Cross and Higgin, *Ber.* 1883, **16**, 1198.

[2] Berthelot, *Compt. Rend.* 1881, **93**, 613.

[3] Brunn, *Ber.* 1889, **22**, 3205.

salt precipitates the metal, the arsenic entering into solution in the form of arsenious acid:—

$$2AsH_3 + 12AgNO_3 + 6H_2O = 2H_3AsO_3 + 12HNO_3 + 12Ag.$$

A very small quantity of arsine can, in this way, be detected by the precipitation of finely divided silver from the clear solution, the liquid becoming acid at the same time. When, on the other hand, arsine is passed into a strong solution of silver nitrate, a yellow coloration is produced which is due to the formation of a double salt, $AsAg_3,3AgNO_3$:—

$$AsH_3 + 6AgNO_3 = AsAg_3,3AgNO_3 + 3HNO_3.$$

On the addition of water this substance is decomposed with formation of arsenious acid and nitric acid, metallic silver being precipitated.[1]

If arsine be passed into a solution of mercuric chloride, a yellow compound, $AsH(HgCl)_2$, is first formed, which changes on further treatment into the brown compound, $As(HgCl)_3$, and finally into black mercury arsenide, As_2Hg_3.[2]

One volume of water absorbs about five volumes of the gas, and the solution on exposure to the air deposits arsenic. Chlorine decomposes arsine with great violence; bromine and iodine also act upon it, but less energetically. Sulphuretted hydrogen does not act upon the pure gas, but in the presence of oxygen or at a temperature above 230° the yellow sulphide of arsenic is formed.[3]

SOLID HYDROGEN ARSENIDE, As_2H_2.

399 This substance is formed as a brown silky mass when sodium arsenide, $AsNa_3$, is decomposed by water.[4] The brown powder produced by leaving the gaseous compound in contact with moist air, or by decomposing one part of arsenic and five of zinc by hydrochloric acid, which was formerly supposed to be this substance, has been shown to be nothing but the element in a finely divided state.

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[1] Poleck and Thümmel, *Ber.* 1883, **16**, 2438.

[2] Partheil and Amort, *Ber.* 1898, **31**, 594.

[3] Brunn, *Ber.* 1889, **22**, 3202.

[4] Janowsky, *Ber.* 1873, **6**, 220.

According to Ogier[1] a solid hydride of the formula As_2H is formed by the action of the electric current on arsine.

ARSENIC AND THE HALOGENS.

400 *Arsenic Trifluoride*, AsF_3.—This compound was obtained by Unverdorben[2] by distilling a mixture of four parts of arsenious oxide and five parts of fluor-spar with ten parts of sulphuric acid. It is a transparent colourless liquid boiling at 63° and having a specific gravity of 2·73; it fumes strongly in the air, has a pungent and powerful odour, and when brought in contact with the skin produces serious wounds which only heal after a long time (Dumas). It attacks glass, and is decomposed by water into arsenious and hydrofluoric acids. It is soluble in ammonia, and forms with this gas a crystalline compound.

Arsenic Pentafluoride is not known in the free state. Marignac, however, obtained a double compound, $AsF_5 + KF$, in colourless crystals by dissolving potassium arsenate in hydrofluoric acid.

401 *Arsenic Trichloride*, $AsCl_3$.—This compound was first prepared by Glauber; his work, "*Furni novi philosophici*," published in the year 1648, contains the following recipe:—"Ex arsenico et auripigmento to distil a butter or thick oil. As has been described under antimony, so likewise from arsenicum or auripigmentum with salt and vitriol can a thick oil be distilled."

Preparation.—In order to prepare arsenic trichloride according to this plan, 40 parts of arsenious oxide must be heated with 100 parts of sulphuric acid to the boiling point of water in an apparatus which is connected with a well-cooled receiver. Small pieces of fused sodium chloride are then carefully thrown in. The decomposition which takes place is as follows:—

$$12HCl + As_4O_6 = 4AsCl_3 + 6H_2O.$$

The water, which is formed at the same time, remains behind in combination with the sulphuric acid, whilst the trichloride distils over.

The same compound is easily obtained by passing dry chlorine over heated arsenic, which burns forming chloride of arsenic. In order to purify it from excess of chlorine it must be rectified over some more arsenic. It may also be prepared by heating

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[1] *Compt. Rend.* 1879, **89**, 1068.

[2] *Pogg. Ann.* 1826, **7**, 316; see also Moissan, *Compt. Rend.* 1884, **99**, 874.

together sulphur monochloride and arsenious oxide in a flask with a reflux condenser, when the following reaction takes place :—

$$As_4O_6 + 6S_2Cl_2 = 4AsCl_3 + 3SO_2 + 9S.$$

On cooling, the sulphur separates out, and the arsenic trichloride may be decanted off.[1]

Properties.—Arsenic trichloride is a colourless oily liquid and has a specific gravity of 2·205 (0°/4°). It solidifies at −18° in pearly needles[2] and boils at 130°·2 (Thorpe), evolving a colourless vapour, which has a specific gravity of 6·3 (Dumas). It is an extremely powerful poison, and evaporates in the air with the emission of dense white fumes. When arsine is led into the liquid, arsenic separates out (Janowsky), thus :—

$$AsCl_3 + AsH_3 = As_2 + 3HCl.$$

When brought in contact with a small quantity of water, stellate groups of needles of arsenic oxychloride, $As(OH)_2Cl$, separate out (Wallace). In contact with a large quantity of water, it decomposes into arsenious oxide and hydrochloric acid, and when the solution is distilled, arsenic trichloride comes over together with the vapour of water; this explains the fact that the hydrochloric acid prepared from arsenical sulphuric acid invariably contains arsenic.

Arsenic pentachloride, $AsCl_5$, is stated to be formed by the action of chlorine on the trichloride at very low temperatures,[3] but according to Smith and Hora[4] this is simply a solution of chlorine in the trichloride.

402 *Arsenic Tribromide*, $AsBr_3$.—In order to prepare this compound, powdered arsenic is added to a solution of one part of bromine in two parts of carbon bisulphide until the solution becomes colourless. Bromine and arsenic are then added alternately until the colour of the first disappears, the clear liquid is poured off, and the bisulphide of carbon allowed to evaporate spontaneously.

Arsenic tribromide forms colourless deliquescent crystals which possess a strong arsenical odour (Nicklès) and melt at about 20°. It has a specific gravity of 3·66 and boils at 220°.

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[1] Oddo and Sena, *Gazzetta*, 1899, **29**, ii, 355.
[2] Besson, *Compt. Rend.* 1889, **109**, 940.
[3] Baskerville and Bennett, *J. Amer. Chem. Soc.* 1902, **24**, 1070.
[4] *J. Amer. Chem. Soc.* 1904, **26**, 632.

By the action of water it is decomposed in a similar way to the chloride.

Arsenic trichloride may be partially converted into the tribromide by heating it with potassium bromide in a sealed tube at 180—220°.[1]

403 *Arsenic Di-iodide*, AsI_2.—When arsenic tri-iodide is heated with arsenic together with a little carbon bisulphide in a sealed tube, arsenic di-iodide is formed, and the same compound is produced when arsenic is heated with iodine in the proper proportions at 230° in a sealed tube. It crystallises from carbon bisulphide in cherry-red, brittle prisms, and easily oxidises in the air. When heated with water or alkalis it turns black, arsenic and the tri-iodide being formed.[2]

Arsenic Tri-iodide, AsI_3.—When arsenic and iodine are brought together they combine with considerable evolution of heat. For the purpose of preparing the tri-iodide a method is adopted similar to that employed for the preparation of the tribromide. It is obtained in the form of bright red hexagonal tables, which have a specific gravity of 4·39. It may also be prepared by passing hydriodic acid into arsenic trichloride, when hydrochloric acid is evolved and the iodide separates out in the form of crystals, or by adding a hot solution of arsenious oxide in hydrochloric acid to a concentrated solution of potassium iodide,[3] whilst if arsenic trichloride and potassium iodide be heated together at 240° in a sealed tube, the following reaction takes place:[4]—

$$AsCl_3 + 3KI = AsI_3 + 3KCl.$$

When it is heated in the air or in oxygen it burns with formation of arsenious oxide. When ammonia is passed through its solution in ether or benzene, a compound of the formula $2AsI_3 + 9NH_3$ is formed, whilst on heating with alcohol to 150°, ethyl iodide, C_2H_5I, is formed.[5] It is used in medicine as a remedy for certain skin diseases.

Arsenic Penta-iodide, AsI_5, has been prepared [6] by heating the tri-iodide with iodine at 150°. It is a brown crystalline mass which melts at 70°, has a sp. gr. of 3·93, and is soluble in water and alcohol. The solutions deposit the tri-iodide on standing.

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[1] Snape, *Chem. News*, 1896, **74**, 27.

[2] Bamberger and Phillipp, *Ber.* 1881, **14**, 2643.

[3] *Ibid.*

[4] Snape, *Chem. News*, 1896, **74**, 27.

[5] Bamberger and Phillipp, *Ber.* 1881, **14**, 2643.

[6] Sloan, *Chem. News*, 1882, **46**, 194.

OXIDES AND OXYACIDS OF ARSENIC.

Arsenic unites with oxygen in two proportions producing two acid-forming oxides, which correspond in composition with the oxides of phosphorus, viz:—

Arsenious oxide, As_4O_6.
Arsenic pentoxide, As_2O_5.

ARSENIOUS OXIDE, OR ARSENIC TRIOXIDE, $As_4O_6 = 361 \cdot 1$.

404 Arsenious oxide has long been known under the names of white arsenic and arsenious acid. In the writings of Basil Valentine the name Hüttenrauch, or smelting-furnace-smoke, is given to this substance because it is obtained by roasting arsenical pyrites, and is emitted during the process in the form of a white smoke which condenses to a white powder.

Arsenious oxide is prepared on the large scale in many metallurgical processes by the roasting of arsenical ores (mispickel, tin ores, &c.). The vapours of the oxide which are given off are now condensed in long passages or chambers called in Silesia poison-chambers (Giftkanäle), formerly in towers termed poison-towers (Giftthürme), in the form of crude flowers of arsenic or poison-flower (Giftmehl). For the preparation of white arsenic, arsenical pyrites is usually employed. It is obtained as a by-product in the roasting of cobalt ores, which are employed in the manufacture of smalt. The crude sublimate obtained in the Freiberg works contains about 75 per cent. of arsenious oxide. Reverberatory furnaces are now supplanting the muffle furnaces in which the operations were formerly conducted. The hearth of the former furnace is about 4 metres in length and about 2·8 metres in breadth, and in it 900 kilos. of the ore can be roasted at once; four charges are made during the day, and the white powder which comes off collects in long underground passages of some 200 metres in length. Large quantities of white arsenic are manufactured in the Harz, in Devonshire and Cornwall, and also at Swansea. The total amount of white arsenic obtained at the mines of the United Kingdom has gradually diminished from 8,129 tons in the year 1885 to 2,131 tons in 1902.

Oxland's self-acting calciner has also been much used for the manufacture of arsenious oxide from the Cornish and Devonshire ores. This furnace consists of an iron tube, from three to six feet in diameter, and thirty feet long, set at an inclination of from half to one inch per foot, varying according to the nature of the ore. This tube is heated by a fire placed at its lower end, whilst at its upper end it is placed in connection with the flues in which the white arsenic is deposited. The tube is made to revolve by suitable machinery at the rate of about one revolution in four minutes, and the crushed ore is admitted in a regular stream through a feed-pipe at the upper end of the tube. Great economy of fuel is effected by this furnace; indeed, if properly worked with a good ore, the heat of combustion of the sulphur and arsenic is itself sufficient to carry on the process. One such cylinder turns out from twenty to twenty-five tons of ore per diem, and the calcined product contains less than 0·5 per cent. of arsenic.[1]

A part of the arsenious oxide comes into the market in the form of a white crystalline powder, the rest in the form of arsenic glass, or amorphous arsenic obtained from the powder by resublimation. For this purpose the arsenic powder which is not white enough to be sent into the market is, in the German manufactories, placed in iron pots heated by a furnace and cylinders placed over them, in which the arsenious oxide condenses in the vitreous form (Glasmachen). The pots hold 4½ cwts. of the crude arsenious oxide, and this is sublimed in from ten to twelve hours. In order to produce a pure product two sublimations are necessary. In this operation care must be taken that a reduction to the state of metallic arsenic does not occur, as this not only colours the arsenic-glass of a dark tint, but is apt to form a fusible alloy with the iron of the pots, and thus to destroy them; if this occurs the oxide then falls into the furnace and escapes into the air, and this is a continual source of danger to the workmen employed in the operation. In England a common reverberatory furnace is used for the resublimation of the crude white arsenic, but, to prevent discoloration by smoke, either coke or anthracite is used (Phillips).

Properties.—Arsenious oxide possesses no smell, but has a weak metallic sweetish taste; it forms a colourless and odourless vapour which has a density of 197·7 at temperatures varying from 570 (Mitscherlich) to 1560° (V. and C. Meyer).[2] Hence its molecular formula is As_4O_6. At a temperature of 1770°, however, it is

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[1] For further particulars see *Handbook of Metallurgy*, Schnabel and Louis, 1898, vol. ii. 480.

[2] *Ber.* 1879, **12**, 1116.

dissociated into As_2O_3.[1] The vitreous modification of arsenious oxide is translucent or transparent, and perfectly amorphous. Its specific gravity is 3·738. On heating, it melts without volatilisation at a temperature of about 200°. When kept for any length of time it becomes opaque, being changed into a porcelain-like mass. This change is due to the passage from the amorphous or vitreous to the crystalline condition; the change commences at the outside of the mass, and gradually penetrates into the interior.

Arsenious oxide is slightly soluble in water. It is deposited on cooling from a hot saturated solution in transparent regular octahedra. It is very much more soluble in hydrochloric acid than in water, and it may be easily obtained from the solution in the form of large crystals. It also occurs in this form as arsenic-bloom, being found together with native arsenic, having been formed by the oxidation of this substance. The naturally occurring crystals sometimes assume the form of octahedra and sometimes of tetrahedra. The specific gravity of octahedral arsenious oxide is 3·689, and in its passage into the amorphous modification an amount of heat is evolved represented by 5,330 thermal units (Deville and Troost). When the crystals are deposited from hydrochloric acid solution, a bright and continuous luminosity is observed in the dark; this, however, does not occur on crystallising a second time. Water and alcohol dissolve different quantities of the amorphous and of the crystalline varieties of the oxide. Thus 80 parts of cold water dissolve 9 parts of the crystalline modification, whilst 1 part of the amorphous variety dissolves in twenty-five parts of water (Bussy). One part of the crystallised oxide requires 400 parts of absolute alcohol for solution, whilst the amorphous variety dissolves in 94 parts of alcohol (Giradin). A constant solubility of each variety at different temperatures cannot, however, easily be obtained, as the two modifications pass readily from one into the other. When the crystallised oxide is heated it evaporates at 125°—150° without melting, but under an increased pressure it melts and passes into the amorphous modification.

Arsenious oxide also occurs in a third form in which it is found crystallised in rhombic prisms, first observed by Wöhler in a deposit from a cobalt roasting-furnace. Claudet found this same modification in a mineral occurring at San Domingo

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[1] Biltz, *Math. natw. Mitt. Berlin.* 1895, 35.

in Portugal, and hence this substance has received the name of claudetite. According to Groth, the relations of the axes of this form are 0·3758 : 1 : 0·3500. This rhombic form of the oxide is formed when a boiling solution of potash is saturated with the amorphous oxide, and the solution allowed to cool (Pasteur). Debray has observed that both crystalline forms may be obtained by heating the oxide in a closed glass tube, half of which is heated to a temperature of 400°. On cooling, the lower part of the tube is found to contain glassy arsenious oxide, the middle part rhombic crystals, and the upper part regular octahedral crystals.

Arsenious oxide unites with many substances to form double compounds. Thus, when dissolved in sulphuric anhydride mixed with different amounts of water, compounds of one molecule of the oxide, As_4O_6, with 16, 8, 4, and 2 molecules of sulphuric anhydride are formed,[1] whilst when heated with sulphuric anhydride compounds with 12 and 6 molecules are obtained.[2] These compounds are very unstable and are decomposed by water. Many similar double compounds with other substances have also been described.

Arsenious oxide serves for the preparation of a large number of other arsenic compounds, especially of the acids of arsenic and their salts. It is also employed in the manufacture of arsenical pigments and is largely used in the manufacture of glass.

ARSENIOUS ACID, $As(OH)_3$.

405 An aqueous solution of arsenious oxide has an acid reaction, and contains tribasic arsenious acid. This has, however, not been prepared in the pure state, although a large number of well-defined salts is known. The salts, which are very stable, are termed the *arsenites*, and of these there are several series known.[3] The most important are: the ortho-arsenites, such as silver ortho-arsenite, Ag_3AsO_3, and calcium ortho-arsenite, $Ca_3(AsO_3)_2$. Then we are acquainted with metarsenites, such as potassium metarsenite, $KAsO_2$; and besides these, other salts are known, such as calcium pyroarsenite,

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[1] Adie, *Journ. Chem. Soc.* 1889, 157.

[2] Weber, *Ber.* 1886, **19**, 3185.

[3] Stavenhagen, *J. pr. Chem.* 1895, [2], **51**, 1.

$Ca_2As_2O_5$, whilst arsenites form double salts with sulphates, chromates, and other compounds.[1]

The arsenites of the alkali metals are soluble in water; those of the other metals insoluble, but easily soluble in acids. A neutral solution of an arsenite produces with ferric chloride a reddish-brown precipitate, with silver nitrate a yellow precipitate, and with copper sulphate a grass-green precipitate. The last is soluble in caustic soda, and when the solution is boiled cuprous oxide, Cu_2O, is precipitated. Oxidising agents convert arsenious into arsenic acid. Thus, for instance, all the elements of the chlorine group effect the change:

$$As(OH)_3 + I_2 + H_2O = AsO(OH)_3 + 2HI.$$

Hence, arsenious acid is often employed for the volumetric determination of chlorine, bromine, and iodine, and of substances which are capable of liberating these elements from their compounds, whilst arsenious acid is often estimated by titration with iodine.

Arsenious oxide and the soluble arsenites act as very powerful poisons, a dose of 0·06 gram (one grain) being very dangerous, whilst one of 0·125 to 0·25 gram (2—4 grains) almost always produces fatal effects unless speedily ejected from the system by vomiting, or at once rendered harmless by its precipitation as an insoluble compound. In small doses, however, arsenious oxide and the arsenites of the alkali metals are largely used in medicine, especially in skin diseases, nervous complaints, and in intermittent fevers. Fowler's solution or the *liquor arsenicalis* of the pharmacopœia is made by dissolving eighty grains of arsenious acid (arsenious oxide) with the same weight of potassium carbonate in one pint of water. The solution then contains four grains of arsenious oxide in one fluid ounce.

It is a very singular fact that persons can accustom themselves to sustain the action of quantities of arsenic which if taken without preparation would certainly prove fatal. Well-authenticated cases of such arsenic-eating occur especially in Styria.[2] In one case, a woodcutter was seen by a medical man to eat a piece of pure arsenious oxide weighing 4·5 grains, and

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[1] Stavenhagen, *Zeit. angew. Chem.* 1894, 165. Friedheim, *Zeit. anorg. Chem.* 1894, **6**, 271 and 273. Reichard, *Ber.* 1894, **27**, 1019.

[2] Roscoe, "On the Alleged Practice of Arsenic-eating in Styria."—***Memoirs of the Lit. and Phil. Soc. of Manchester.*** 1860.

the next day he crushed and swallowed another piece weighing 5·5 grains, living on the following day in his usual state of health. The reasons which the arsenic-eaters give for the practice, which is usually carried on in secret, is that it enables them to bear heavy weights with ease to great elevations. The workmen in the arsenic works also appear to possess the power of withstanding doses of arsenic which, given to ordinary persons, would produce fatal effects.

As an antidote against arsenic poisoning, sulphuretted hydrogen was formerly employed, but this substance does not act satisfactorily. Bunsen and Berthold proposed the best antidote for poisoning by arsenic, namely, freshly precipitated hydrated oxide of iron.[1] This converts the soluble arsenious acid or even an alkali arsenite into basic ferric arsenite insoluble in water and in the liquids of the stomach. The hydrated oxide should be freshly prepared, as when kept it becomes crystalline and loses its power.

ARSENIC PENTOXIDE, $As_2O_5 = 228·2$.

406 Arsenic is distinguished from phosphorus, which it otherwise closely resembles chemically, inasmuch as when burnt in the air or in oxygen it oxidises to arsenious oxide which does not directly combine with more oxygen. If, however, the arsenious oxide be treated with an oxidising agent in presence of water, arsenic acid, $AsO(OH)_3$, is formed, and this, when heated to a temperature slightly below a red heat, gives off water, and arsenic pentoxide remains behind as a white porous mass:—

$$2AsO(OH)_3 = As_2O_5 + 3H_2O.$$

If the substance be heated still more strongly, it melts and decomposes into arsenious oxide and oxygen.

The specific gravity of arsenic pentoxide is 3·734 (Karsten); it dissolves slowly, but to a considerable extent, in water, and deliquesces in moist air with formation of arsenic acid. It is easily reduced to free arsenic when heated in presence of charcoal, potassium cyanide, or other reducing agents.

ARSENIC ACID, $AsO(OH)_3$.

407 Arsenic acid was first prepared by Scheele, in the year 1775, by dissolving arsenious oxide in aqua regia, and also by

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[1] *Das Eisenoxydhydrat, das Gegengift der arsenigen Säure.* Göttingen. 1834.

acting with chlorine upon this oxide in the presence of water, thus:—

$$As_4O_6 + 10H_2O + 4Cl_2 = 4AsO(OH)_3 + 8HCl.$$

Arsenic acid is also formed very readily when the lower oxide is warmed with nitric acid, and this is the process which is employed for the manufacture of the substance on the large scale. Nitrous fumes escape, and pass, together with air, up a tower filled with coke, where they meet a current of water; they are thereby oxidised to nitric acid which is condensed.

Arsenic acid as it appears in commerce is a thick, very acid liquid, having a specific gravity of 2·0. It deposits, when cooled, transparent crystals having the formula $2AsO(OH)_3 + H_2O$. These crystals melt at 100°, and give off water, the anhydrous *ortho-arsenic acid*, H_3AsO_4, remaining behind as a crystalline powder. Arsenic acid possesses a very acid and unpleasantly metallic taste, and acts as a poison, though not so powerful a one as the trioxide.[1] The concentrated solution of the acid acts on the skin as a strong cautery. Heated to a temperature of 180°, it loses water, and hard, glittering crystals of *pyro-arsenic acid*, $H_4As_2O_7$, separate out. This on heating to 200° again loses water, a white crystalline mass of *metarsenic acid*, $HAsO_3$, being left. The pyro- and meta-acids both dissolve in water with evolution of heat, and are transformed at once into the ortho-acid. This property serves to distinguish these two varieties from the corresponding forms of phosphoric acid, both of which can be obtained in solution.

Crystals of the formula $As_2O_5 + 4H_2O$, melting at 35°—36°, may be obtained from a syrup of the same composition,[2] whilst the hydrate, $2As_2O_5 + 3H_2O$, is formed on heating an aqueous solution of arsenic acid for three days at 63°.[3]

The specific gravity of aqueous solutions of arsenic acid of known strength is, according to the experiments of Schiff,[4] as follows:—

Specific Gravity.	Percentage of H_3AsO_4.	Specific Gravity.	Percentage of H_3AsO_4.
1·7346	67·4	1·1606	22·5
1·3973	45·0	1·1052	15·0
1·2350	30·0	1·0495	7·5

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[1] Wöhler and Frerichs, *Annalen*, 1848, **65**, 335.

[2] Joly, *Compt. Rend.* 1885, **101**, 1262.

[3] Auger, *Compt. Rend.* 1902, **134**, 1059.

[4] *Annalen*, 1861, **113**, 183.

Arsenic acid is completely reduced to arsenious acid by warming with an aqueous solution of sulphurous acid.

The Arsenates.—The salts of arsenic acid, or the arsenates, are isomorphous with the corresponding phosphates. Indeed, it was by the comparison of these two series of salts that Mitscherlich in the year 1819 was led to the discovery of the law of isomorphism. In their reactions, as well as in their general properties, these two classes of salts exhibit great analogy. Thus the soluble arsenates give, with ammonia, ammonium chloride and a magnesium salt, a crystalline precipitate of $MgNH_4AsO_4+6H_2O$, corresponding exactly to the phosphorus compound; and when gently warmed with a solution of ammonium molybdate in nitric acid, the arsenates give a yellow precipitate similar to that obtained with a phosphate. They may, however, be distinguished from the latter class of salts, inasmuch as a neutral solution produces with silver nitrate a dark reddish-brown precipitate, and when acetate or nitrate of lead is added to a neutral solution a white precipitate of lead arsenate, $Pb_3(AsO_4)_2$, is obtained, and this when heated on charcoal before the blowpipe is reduced to arsenic, which emits its peculiar garlic-like smell.

Being tribasic, arsenic acid forms three series of salts. Of the normal salts only those of the alkali-metals are soluble in water. Two series of acid-salts or hydrogen-salts also exist, such as Na_2HAsO_4, and NaH_2AsO_4. The former of these salts when carefully heated yields sodium pyro-arsenate, $Na_4As_2O_7$, and the latter sodium metarsenate, $NaAsO_3$. These salts can, however, only exist in the solid state, as when they are dissolved in water they are at once transformed into the ortho-compounds.

Arsenic acid is used largely in commerce in the manufacture of magenta; and its salts, especially sodium arsenate, are employed to a great extent in the processes of calico-printing.

ARSENIC AND THE ELEMENTS OF THE SULPHUR GROUP.

408 Arsenic forms the following compounds with sulphur, viz.:—

Arsenic subsulphide, As_3S;
Arsenic disulphide or realgar, As_2S_2;
Arsenic trisulphide or orpiment, As_2S_3;
Arsenic pentasulphide, As_2S_5.

Of these, the last two correspond to the oxides, and act as acid-forming sulphides, giving rise to well-defined series of salts termed the thio-arsenites and thio-arsenates.

ARSENIC SUBSULPHIDE, As_3S.

This compound is obtained[1] by adding phosphorus trichloride to an aqueous solution of sodium arsenate, allowing the mixture to cool, saturating with sulphur dioxide, and allowing the whole to stand for two or three days, when a dark brown precipitate of arsenic subsulphide separates out.

This sulphide, on heating, decomposes, giving realgar which sublimes, and arsenic which remains behind.

It is soluble in yellow ammonium sulphide, forming a solution from which arsenic trisulphide is precipitated on acidification.

ARSENIC DISULPHIDE, As_2S_2.

409 This compound occurs native as realgar, crystallising in oblique prisms belonging to the monoclinic system. These possess an orange-yellow colour and resinous lustre, and are more or less translucent; the streak varies from orange-yellow to red. The specific gravity is 3·4 to 3·6, and hardness 1·5 to 2·0. It occurs together with silver and lead ores at Andreasberg in the Harz and other localities, and embedded in dolomite on the St. Gothard, and has been found in minute crystals in Vesuvian lavas. Strabo mentions the occurrence of "Sandaraca" in a mine in Paphlagonia.

When it is heated to 150° with a solution of sodium bicarbonate it dissolves in the liquid and afterwards separates out in the crystalline form (Sénarmont).

The red arsenic glass or ruby sulphur which occurs in commerce is an artificial disulphide of arsenic prepared in various arsenic works. In Freiberg, arsenical pyrites and common pyrites are used for this purpose, mixed in such proportions that the mixture contains about 15 per cent. of arsenic and 27 per cent. of sulphur. Such a mixture is then sublimed in a furnace in which are placed twelve iron tubes. Each tube holds about thirty kilograms of the ore, and the charge is renewed every twelve hours. In order to give the product the right degree of colour it is again melted with sulphur.

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[1] Scott, *Journ. Chem. Soc.* 1900, 651.

Ruby sulphur is a red glassy mass, translucent at the edges. It does not possess a constant composition: the material manufactured at Freiberg contains generally 75 per cent. of arsenic and 25 per cent. of sulphur, and that made at Reichenstein in Silesia is a mixture of 95 parts of disulphide with 5 parts of sulphur. This body was formerly much used as a pigment, and is still employed in the manufacture of the so-called Indian- or white-fire, which is a mixture of two parts of the disulphide with twenty-four parts of nitre, and burns with a splendid white light when ignited. The disulphide is also employed in tanning, being mixed with lime and employed for removing the hair from the skins.

ARSENIC TRISULPHIDE, As_2S_3.

410 This substance occurs in nature and is known under the name of *orpiment* (auri pigmentum) or the *yellow sulphide of arsenic*, and was known to Pliny as *arsenicum*. It crystallises in translucent lemon-coloured prisms belonging to the monoclinic system, and has a specific gravity of 3·46.

When sulphuretted hydrogen is passed through an aqueous solution of arsenious oxide the liquid becomes of a yellow colour, but no precipitate is formed, the liquid containing arsenic trisulphide in the colloidal form.[1] If a small quantity of hydrochloric acid be present, a beautiful yellow precipitate of arsenic trisulphide is at once thrown down. On heating this substance it melts to a yellowish-red liquid which volatilises without decomposition at a temperature of about 700°. Heated in the air it takes fire and burns with a pale blue coloured flame to arsenious oxide and sulphur dioxide.

It dissolves in solutions of the alkali hydroxides, a brown precipitate of arsenic, containing a little sulphur, separating out slowly, whilst the solution contains thio-arsenate and thio-oxyarsenates.[2]

The sulphide of arsenic occurring in commerce is prepared by subliming a mixture of seven parts of pulverised arsenious oxide with one part of sulphur, and it is really a mixture of arsenious oxide with more or less sulphide of arsenic. The material

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[1] Schulze, *J. pr. Chem.* 1882, [2], **25**, 431; see also Picton, *Journ. Chem. Soc.* 1892, 127, 140; Küster and Dahmer, *Zeit. anorg. Chem.* 1902, **33**, 105.

[2] Weinland and Lehmann, *Zeit. anorg. Chem.* 1901, **26**, 322.

thus prepared, which is very poisonous, from the excess of arsenious oxide which it contains, was formerly much used as a pigment under the name of King's yellow, but it is now almost entirely superseded by the comparatively innocuous chrome yellow. The yellow sulphide of arsenic is also used in the arts and manufactures, for instance in the printing of indigo colours; and a mixture of orpiment, water, and slaked lime is used in the East under the name of Rusma as a depilatory, its action depending upon the formation of a hydrosulphide of calcium.

The Thio-arsenites, M_3AsS_3.—These salts, which are frequently termed the *sulpharsenites*, stand in the same relation to the trisulphide as the arsenites to arsenious oxide. They are formed by the combination of the trisulphide with the sulphide of a metal, and they may be arranged, like the arsenites, in different groups. Acids decompose them with precipitation of the trisulphide. The thio-arsenites of the alkali metals are soluble in water, yielding yellow solutions; those of the other metals exist in the form of coloured precipitates.

ARSENIC PENTASULPHIDE, As_2S_5.

411 When sulphuretted hydrogen is passed through a solution of arsenic acid at some temperature between 4° and 80°, the precipitate consists of arsenic pentasulphide mixed with arsenic trisulphide and sulphur, a partial reduction of the arsenic acid having taken place; whilst thio-arsenic acid and thio-oxyarsenic acids are also formed, and remain in solution.[1]

In the presence of hydrochloric acid, however, and when the gas is passed rapidly into the warm solution, the precipitate consists entirely of the pentasulphide.[2] The pentasulphide can also be obtained by fusing the trisulphide in the proper proportions with sulphur. It forms a yellow fusible mass, which can be sublimed without decomposition in absence of air. It is more readily obtained by acidulating a dilute solution of sodium thio-arsenate with hydrochloric acid (Fuchs):—

$$2Na_3AsS_4 + 6HCl = 6NaCl + 3H_2S + As_2S_5.$$

The thio-arsenates or *sulpharsenates* are formed by dissolving the

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[1] McCay, *Ber.* 1899, **32**, 2471; 1901, **34**, 2166; *Zeit. anorg. Chem.* 1901, **29**, 36.

[2] Brauner and Tomitscheck, *Ber.* 1888, **21**, 221c; Neher, *Zeit. anal. Chem.* 1893, **32**, 45.

pentasulphide in a solution of the sulphide of an alkali-metal or by treating the trisulphide with an alkali polysulphide:—

$$As_2S_3 + K_2S_3 = 2KAsS_3,$$

whilst by boiling sodium arsenite solution with sodium monosulphide a thio-arsenate, Na_3AsS_4, is formed, together with thio-oxyarsenate.[1]

As will be seen by the above formulæ, both ortho- and meta-thio-arsenates exist, and we are likewise acquainted with pyro-thio-arsenates such as $K_4As_2S_7$. The thio-arsenates of the alkali metals are soluble in water, yielding yellow solutions, whereas the corresponding salts of the other metals form insoluble precipitates.

The *thio-oxyarsenates* or *sulphoxyarsenates* are compounds in which the oxygen of arsenic acid is only partially replaced by sulphur, and they are also formed along with thio-arsenates when arsenic pentasulphide is dissolved in alkalis;[2] in this way the crystalline thio-oxyarsenates, $Na_3AsSO_3 12H_2O$ and $Na_3AsS_2O_2 11H_2O$, have been obtained as well as a number of other salts.[3]

Arsenic Chloro- and Iodo-sulphides.

412 Dry sulphuretted hydrogen reacts with arsenic trichloride at ordinary temperatures, and with arsenic tri-iodide at 200°, forming the chlorosulphide, As_2S_5Cl, and the iodo-sulphide, As_2S_5I. This chlorosulphide is also produced when arsenic trisulphide is heated with chlorine out of contact with air, whilst with iodine in place of chlorine the bodies As_2SI and As_2S_2I have been obtained.

Another compound, AsS_2Cl, has been formed by heating arsenic trisulphide and trichloride together in a sealed tube.

These compounds are crystalline, and are decomposed on volatilisation and by boiling water.[4]

413 *Compounds of arsenic with selenium and with tellurium* are stated to be obtained on heating the two elements

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[1] Weinland and Rumpf, *Zeit. anorg. Chem.* 1897, **14**, 42.

[2] Weinland and Lehmann, *Zeit. anorg. Chem.* 1901, **25**, 322; McCay, *Ber.* 1899, **32**, 2471; *Zeit. anorg. Chem.* 1900, **25**, 459.

[3] *Zeit. anorg. Chem.* 1904, **41**, 452.

[4] Ouvraid, *Compt. Rend.* 1893, **116**, 1516; 1893, **117**, 107.

together in the requisite proportions in sealed tubes.[1] The following compounds have been described: with selenium, As_2Se, As_2Se_2, As_2Se_3 and As_2Se_5, and with tellurium, As_8Te_3, As_2Te_2 and As_2Te_3.

The pentaselenide dissolves in alkalis forming selenoarsenates and seleno-oxyarsenates, which are decomposed on acidifying with hydrochloric acid, yielding a brown precipitate of arsenic pentaselenide.[2]

By fusing selenium with arsenic and sulphur or with the sulphides of arsenic the compounds As_2SSe_2, AsS_2Se, $As_2S_2Se_3$ and $As_2S_3Se_2$ have been prepared.[3]

A number of sodium thio-selenoarsenates and thio-seleno-oxyarsenates have also been described.[4]

COMPOUNDS OF ARSENIC WITH NITROGEN AND PHOSPHORUS.

414 *Arsenamide*, $As(NH_2)_3$, is formed, together with ammonium chloride,[5] when arsenic trichloride is saturated at –30° to –40° with ammonia gas:—

$$AsCl_3 + 6NH_3 = As(NH_2)_3 + 3NH_4Cl.$$

Arsenamide is a greyish-white, amorphous powder, insoluble in liquid ammonia; it exists in moist air only below 0°, and at ordinary temperatures only in an atmosphere of ammonia, whilst it is decomposed by water with formation of arsenious oxide and ammonia.

Above 0° it loses ammonia and forms *arsenimide*, $As_2(NH)_3$, thus:—

$$2As(NH_2)_3 = As_2(NH)_3 + 3NH_3,$$

a light yellow, amorphous compound, which like arsenamide is decomposed by water yielding arsenious oxide and ammonia.

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[1] Clever and Muthmann, *Zeit. anorg. Chem.* 1895, **10**, 117; Szarvasy, *Ber.* 1895, **28**, 2654; *Ber.* 1897, **30**, 1244; Szarvasy and Messenger, *Ber.* 1897, **30**, 1343; and *Journ. Chem. Soc.* 1899, 597.

[2] Clever and Muthmann, *Zeit. anorg. Chem.* 1895, **10**, 117; Szarvasy, *Ber.* 1895, **28**, 2654.

[3] von Gerichten, *Ber.* 1874, **7**, 29; Szarvasy, *Ber.* 1895, **28**, 2654.

[4] Clever and Muthmann, *loc. cit.*; Weinland and Rumpf, *Zeit. anorg. Chem.* 1896, **29**, 1006; 1897, **14**, 42; Messenger, *Ber.* 1897, **30**, 797.

[5] Hugot, *Compt. Rend.* 1904, **139**, 54.

This compound may be heated in a vacuum to 100° without alteration, but at 250° ammonia is given off and *arsenic nitride*, AsN, formed:—

$$As_2(NH)_3 = 2AsN + NH_3.$$

Arsenic nitride is an orange-red body which is decomposed at the temperature of formation into arsenic and nitrogen.

ARSENIC PHOSPHIDE, AsP.

415 When dry arsine is led into phosphorus trichloride, the above compound is precipitated in the form of a brownish-red powder. It is slightly soluble in bisulphide of carbon, and is oxidised with ignition when acted upon by nitric acid. Heated in absence of air, it decomposes into its constituents, and when heated with an aqueous solution of an alkali it gives off arsine and phosphine, leaving behind a residue of an arsenite and a phosphite.[1]

THE DETECTION OF ARSENIC IN CASES OF POISONING AND IN FOOD MATERIAL.

416 With a few exceptions, the compounds of arsenic are more or less poisonous. Arsenious oxide is a particularly powerful poison, and as this substance is largely used in the arts and manufactures, and likewise employed on a large scale as a rat- and vermin-poison, it is not difficult, in spite of legislative enactments respecting the sale of poisons (Sale of Poisons Bill), to obtain this compound in quantity, and hence cases of accidental poisoning with this substance are not uncommon, and, in addition, it is too frequently made use of for the express purpose of destroying human life.

In 1900 a serious outbreak of arsenical poisoning occurred, chiefly in the neighbourhood of Manchester, due to the contamination of beer with arsenious acid, and a number of fatalities occurred. The presence of this arsenic in the beer was traced to the use of impure sulphuric acid in the manufacture of the glucose employed in the brewing, which was found to contain considerable quantities of arsenious acid.[2]

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[1] Janowsky, *Ber.* 1873, **6**, 216.

[2] Delepine, *Journ. San. Inst.* 1902, **23**, iii, 244; Report of Commission to the Manchester Brewers' Association, *Analyst*, 1900, **26**, 13; see also Report of the Royal Commission on Arsenic Poisoning in Beer, 1902.

In medico-legal investigations, in cases of poisoning by arsenic, whether it be in the contents of the stomach, in vomited matter, or in the several portions of the body itself, it is not sufficient for the toxicologist to ascertain with certainty the presence of arsenic. He is bound also to determine, with as great a degree of accuracy as is attainable, the absolute amount of this poison found in the body, in order that he may be able to give a distinct opinion as to whether the quantity is sufficient to produce fatal effects. It is the first duty of the chemist who investigates such matters, to ascertain that the whole of the reagents employed as well as the apparatus used in his experiments are altogether free from arsenic. This is especially necessary, as hydrochloric and sulphuric acids, which are invariably employed for the investigation, are very apt to contain traces of arsenic; and inasmuch as arsenic is sometimes present in the glaze of certain kinds of porcelain. The operation which is conducted for the purpose of satisfying the experimenter as to the freedom of his apparatus and chemicals from arsenic is termed a *blank experiment*, and must be carried on with the same quantities of the same materials, and with the same kind of apparatus, side by side with the real experiment in which the substance supposed to contain the poison is examined.

In cases of poisoning with white arsenic, the quantity of the poison employed is almost always more than is necessary to produce death, and, as arsenious oxide is very sparingly soluble in water, white particles may frequently be found either adhering to the coatings of the stomach and intestines, or in the vomit. These white particles must be carefully looked for by help of a lens, amongst the folds and in the inflamed portions of the stomach and intestines as well as in the contents of the stomach itself, and picked out with pincettes, washed with cold water, dried, and then brought into a tube made of hard glass drawn out to a point of the form and size shown in Fig. 163. In the tube, above these dried white particles, a small splinter of ignited wood-charcoal is placed, and then this charcoal heated in the flame. As soon as this is red-hot, the tube, which is at first held in a horizontal direction, is gradually slanted, keeping the charcoal still heated in the flame, and thus brought into a nearly vertical position, so that at last the point of the tube becomes red-hot. The vapour of the trioxide then passes over the red-hot carbon and is reduced to the metal, which is deposited in the form of a bright metallic mirror, shown in Fig. 164, on the part of the tube above the carbon. When cooled, the charcoal is shaken out, and the metallic arsenic is heated by itself so as to drive it up into the wider portion of the tube. If it be not present in large quantity, it is wholly oxidised in the act of volatilisation to the oxide, which forms a white sublimate in the upper part of the tube, consisting, as may be seen with the lens, of small glittering octahedra, shown in Fig. 165. This is then dissolved in a small quantity of boiling water, and, when the solution is cold, a solution of silver nitrate is added, and then very dilute ammonia drop by drop until the liquid is neutral. A yellow precipitate of silver arsenite is then formed:—

FIG. 163.

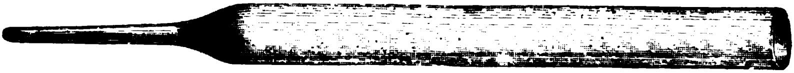

FIG. 164.

$$As_4O_6 + 12AgNO_3 + 12NH_4HO = 4Ag_3AsO_3 + 12NH_4NO_3 + 6H_2O.$$

The arsenious oxide may also be dissolved in warm hydrochloric acid and then sulphuretted hydrogen passed through the solution, when the yellow sulphide of arsenic is precipitated.

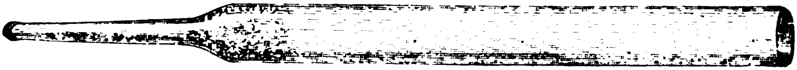

FIG. 165.

If no particles of undissolved arsenious oxide can be found, the organic matter under investigation, which if it consists of the solid portion of the body must be cut up into small pieces, is brought into a retort provided with a well-cooled receiver and containing fused common salt or pure rock salt. This mixture is then distilled with pure sulphuric acid, whereby arsenic trichloride is formed, and this substance volatilises with the vapours of water and hydrochloric acid. In order that this operation should be successful, it is necessary that a smaller quantity of sulphuric acid should be added than that needed to decompose the whole of the salt. The cooled distillate is then treated with sulphuretted hydrogen, and the precipitate, consisting of impure sulphide of arsenic, is treated as hereafter described.

The above method can only be employed when the arsenic is in the state of arsenious oxide, or as an arsenite. In order to ascertain with certainty whether arsenical compounds in general are present, the following method must be adopted.

The contents of the stomach, or solid portions of the stomach or other organs, are obtained in as fine a state of division as possible, and the organic matter destroyed or charred, either by heating on the water-bath with hydrochloric acid to which potassium chlorate is added from time to time (Fresenius and Babo), or by treatment on the water-bath with nitric and sulphuric acids.[1]

The arsenic is then precipitated in the filtered solution with sulphuretted hydrogen, and the impure arsenic trisulphide separated from the sulphides of tin, lead, mercury, &c., that may be present, by dissolving it in ammonia; the filtrate is evaporated down and any organic matter still present is destroyed by heating with nitric and sulphuric acids, and any antimony sulphide removed by fusing with a mixture of sodium nitrate and carbonate, dissolving in a mixture of alcohol and water and filtering off the insoluble sodium antimonate formed. It is then again precipitated with sulphuretted hydrogen, dissolved in ammonia, the solution evaporated down and the residual arsenic trisulphide weighed.[2]

The next operation is to convert the sulphide into metallic arsenic in order to be positively certain that this substance is present. A portion of the weighed precipitate is heated with pure nitric acid, the solution obtained evaporated on the water-bath, and the dry mass dissolved in water. Metallic arsenic is best obtained from this solution, which, of course, contains arsenic acid, by employing the well-known reaction of Marsh.[3]

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[1] Gautier, *Compt. Rend.* 1899, **129**, 936.

[2] For details see Fresenius, *Quantitative Analysis.*

[3] *New Edin. Phil. Journ.* 1836, p. 229.

The apparatus employed for this purpose[1] is seen in Fig. 166 and consists of a flask of 200 c.c. capacity fitted with a tube-funnel and a drying tube containing, first, a roll of blotting-paper soaked in lead acetate solution and dried, then a wad of cotton-wool, some pieces of calcium chloride, and finally another wad of cotton-wool. The end of this tube is connected with a reduction tube of hard glass, part of which is drawn out so as to make a fine tube with a diameter of about 0·092 inch.

Hydrogen is evolved in the flask from a mixture of zinc and dilute hydrochloric or sulphuric acid, great care being taken to have these materials free from arsenic. Before adding the arsenical solution the hydrogen is evolved for twenty minutes, the shoulder of the reduction tube being meanwhile heated to redness, as shown in the figure; if no mirror of arsenic be formed in the fine portion of the tube in this time, the materials may be assumed to be free from arsenic.

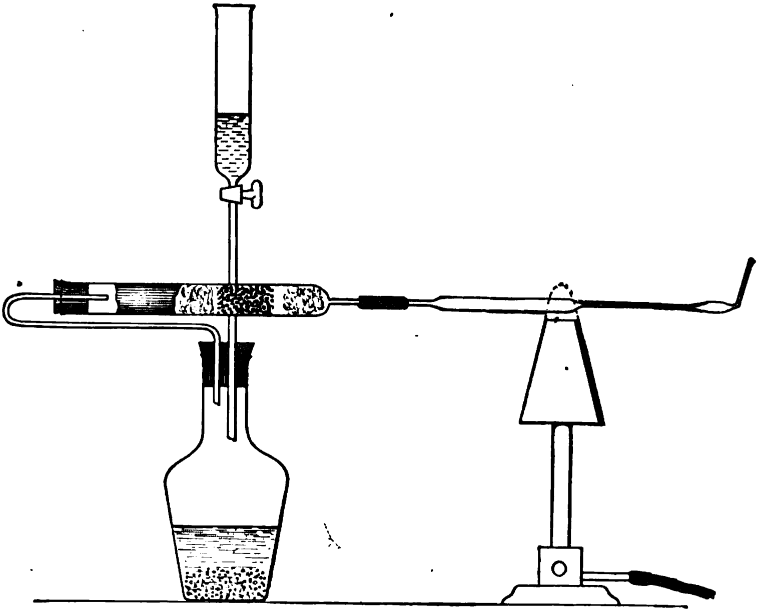

FIG. 166.

The solution under examination is then gradually allowed to run into the flask, and the reduction tube again heated for

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[1] Report of conjoint committee of the Soc. Chem. Ind. and the Soc. Public Analysts, *J. Soc. Chem. Ind.* 1902, **21**, 93.

twenty minutes, when a dark, mirror-like deposit of arsenic collects in the drawn-out portion if arsenic be present.

If care be taken to dilute the arsenic solution sufficiently, the whole of the arsenic is obtained in the form of a mirror, and its amount may be estimated by comparison with a set of standard mirrors prepared with 0·001 to 0·01 mg. of arsenious oxide.

If too much arsenic be added, or if it be not added gradually, some of the arsine escapes, and, if the hydrogen be ignited at the end of the tube, the flame assumes a pale lavender tint and pieces of white porcelain placed in the flame become covered with a dark deposit of arsenic, which is dissolved by sodium hypochlorite solution, the soluble sodium arsenate being formed by oxidation.

To remove any doubt as to whether the mirrors are metallic arsenic, a portion of the tube is broken off and the mirror heated in the flame, when arsenious oxide is formed and volatilises into the cool parts of the tube as a white crystalline sublimate.

For the estimation of arsenic in beer, brewing materials, and foods, the organic matter may be destroyed by heating repeatedly with nitric and sulphuric acids, the residue being extracted with dilute hydrochloric acid, or the material may be used without the oxidation of the organic matter, when it is digested with cold dilute hydrochloric acid, and if sulphites be present they are oxidised by bromine, and the excess of bromine boiled off. The filtrate from either of these methods is then treated in Marsh's apparatus, as already described.

A modification of Reinsch's test[1] has also been used for the estimation of arsenic in beer and foods.[2]

This process consists in adding hydrochloric acid to a known amount of the substance to be tested, placing strips of pure copper in the mixture and heating the whole for a certain length of time. When arsenious acid or its compounds are present a dark deposit of arsenic is obtained upon the copper. The copper is then removed, well washed with water, dried, and heated in a hard glass tube, the arsenic being oxidised and deposited as arsenious oxide in a ring on the cool part of the tube. The amount may be estimated by comparison with

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[1] *Schweig Journ.* **53**, 377.

[2] Delepine, *Journ. San. Inst.* 1902, **23**, iii, 244. For further work on the detection and estimation of arsenic see Reports of the Royal Commission on Arsenical Poisoning.

standard tubes, made by adding known amounts of arsenic to arsenic-free beer or food and treating the mixture in the same manner.

When only very minute traces of arsenic are present the copper is heated in a metal thimble over which is placed a microscope slide, and the deposit produced on the slide is compared under the microscope with standards prepared in the same manner.

By this means Delepine has estimated 1 part of arsenious acid in 10,000,000 parts of beer.

The hydrogen required for Marsh's method may also be prepared electrolytically. This method, due to Thorpe, and in use in the Government laboratory, depends upon the fact that when hydrogen is evolved electrolytically in the presence of arsenious acid or its salts arsine is formed. Arsenates are not reduced in this way and must be reduced to arsenites before being treated by this method.

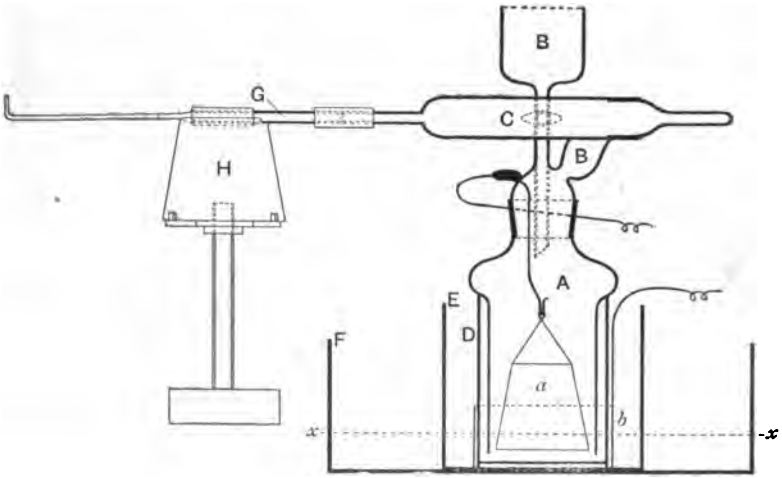

Fig. 167.

The apparatus used is shown in Fig. 167 and consists of a glass vessel *A* open at the bottom, and fitting loosely into a porous cell *D* containing dilute sulphuric acid, in which is suspended the cathode (*a*) of sheet platinum in the form of a perforated cone, and into which the arsenical solution is run through the tap-funnel *B*. The anode consists of a band of platinum passing loosely round the porous cell, and immersed in dilute sulphuric acid in the vessel *E*, the whole being cooled by an outer vessel containing cold water.

The arsine passes up into the vessel *A*, then through the drying tube *C*, the gas being decomposed as before by heating the hard glass combustion tube; a piece of platinum gauze is wrapped round the tube at the point where it is heated, to prevent the softening of the tube.

In performing the estimation a little amyl alcohol is first run in, and then the whole of the liquid under examination, which has been prepared as already described, is run in at once; the mirrors produced after thirty minutes' heating are compared with standards prepared in exactly the same manner.[1]

It has already been remarked that arsenious oxide is employed largely for the manufacture of Scheele's green and emerald green, and that arsenic acid is employed on a very large scale in the manufacture of the aniline colours. The employment of arsenical wall-papers is much to be deprecated; still more is the employment of the insoluble arsenical green for colouring light cotton fabrics, such as gauze, muslin, or calico, to be condemned. The colour is merely pasted on with size, and rubs off with the slightest friction.

Several moulds, especially *Penicillium brevicaule*, when grown in the presence of arsenious oxide evolve a strongly odorous gas stated to be diethyl-arsine, and this has been proposed as a method of detecting arsenious acid (Gosio).[2]

It is to these moulds that the evil effects produced by arsenical wall-papers are attributed; at the same time arsenic doubtless finds its way into the system in the form of dust, which in such rooms invariably contains it.

For the purpose of detecting arsenic in wall-papers or cotton fabrics, the colour is dissolved in hydrochloric acid, and the solution submitted to the Reinsch test.

BORON. B = 10· (H = 1).
= 11·0 (O = 16).

417 Boron does not occur in nature in the free state, but is found combined with hydrogen and oxygen, forming boric or boracic acid, $B(OH)_3$, and its salts. Of these latter the most

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[1] Thorpe, *Journ. Chem. Soc.* 1903, 974.

[2] See also Morgan, *Lancet*, 1903, **2**, 22, where the literature is cited.

important are tincal or native borax, $Na_2B_4O_7+10H_2O$, boracite, $2Mg_3B_8O_{15}+MgCl_2$, and borocalcite, $CaB_4O_7+4H_2O$.

The name borax is found in the writings of the Latin Geber and other alchemists. It is, however, doubtful whether they understood by the word the substance which we now denote by it. Nothing satisfactory was known concerning the chemical nature of this salt for a long time. Homberg[1] first prepared boric acid from borax in the year 1702, and he termed it *sal sedativum*, for he was unacquainted with the composition of the acid. It was not till 1747–8 that Baron showed in two memoirs read before the French Academy that borax was a compound of *sal sedativum* and soda. After the establishment of the Lavoisierian system, the name boracic acid was given to *sal sedativum*, and it was then assumed that this acid contained an unknown element, for the isolation of which we are indebted to Gay-Lussac and Thénard,[2] as well as to Davy,[3] who about the year 1808 obtained elementary boron.

Boron occurs in two allotropic modifications: amorphous and crystalline.

Amorphous Boron.—This modification was obtained by Gay-Lussac by heating boron trioxide, B_2O_3 (obtained by the ignition of boric acid), with potassium in an iron tube. It may also be obtained by mixing ten parts of coarsely powdered boron trioxide with six parts of sodium, bringing the mixture into a crucible already heated to redness, and covering it with a layer of powdered sodium chloride previously well dried. As soon as the reaction, which is very violent, has subsided, the mass is stirred with an iron rod until all the sodium has been oxidised, and then carefully poured into water acidified with hydrochloric acid. The soluble salts dissolve in the water, whilst the boron remains behind as an insoluble brown powder. This is then collected on a filter, and it must be very carefully dried, as it is easily oxidised and may take fire.

The boron obtained in this way is impure, and a similar product is got when boron trioxide or borax is heated with magnesium powder. In this case a boride of magnesium is probably formed of the formula Mg_2B_5, which is decomposed by acids. The product left after this treatment, however, still contains about 5 per cent. of magnesium and about 1 per cent. of hydrogen, which is also found in boron prepared by means

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[1] *Crell. Chem. Archiv.* **2**, 265.

[2] *Recherches*, i. 269.

[3] "Decomposition of Boracic Acid," *Phil. Trans.* 1809, i. 75.

of sodium, and is probably present in the form of a solid hydride.

In order to prepare pure boron, 70 gr. of magnesium powder are heated with 210 gr. of boron trioxide. The product, which consists of boron, accompanied by magnesium boride and borate, is treated with dilute acid which dissolves the borate and the greater part of the boride. In order to remove the last portions of the boride the residue is then fused with borax and again treated with hydrochloric acid, which leaves the boron containing only traces of silicon, iron, and magnesium. The presence of nitride of boron in the final product can only be avoided by carrying out the heating in an atmosphere of hydrogen or by placing the mixture in a crucible lined with titanic acid.[1]

Amorphous boron is a chestnut-brown powder of specific gravity 2·45. It is infusible even at the temperature of the electric arc, but volatilises, the extremities of the electrodes being converted into boron carbide,[2] whilst if it be heated to 700° in air it burns. It is a more powerful reducing agent than carbon or silicon, inasmuch as it is oxidised by carbonic oxide and by silica. It combines with bromine at 700°, but not with iodine, and forms compounds with many metals on heating, among which are silver and platinum, whilst on fusing with cast-iron in a current of hydrogen it replaces the carbon giving a white, hard cast-iron,[3] and if fused with reduced iron produces brown steel.[4] It is acted on by the oxy-acids, is oxidised by water vapour, and combines with nitrogen at a high temperature.[5] It is a non-conductor of electricity, and when freshly prepared and not strongly ignited is slightly soluble in water, imparting to it a yellow colour and being precipitated unchanged from its aqueous solution on the addition of acids or salts.

418 *Crystalline or Adamantine Boron.*—This substance was first obtained in the year 1856 by Wöhler and Deville.[6] It can be prepared by several processes. Thus, if amorphous boron be pressed down tightly in a crucible, a hole bored in the centre of the pressed mass, a rod of aluminium dropped into the hole,

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[1] Gattermann, *Ber.* 1889, **22**, 195; Winkler, *Ber.* 1890, **23**, 772; Lorenz, *Annalen*, 1888, **247**, 226.

[2] Moissan, *Compt. Rend.* 1893, **117**, 43.

[3] Moissan, *Compt. Rend.* 1894, **119**, 1172.

[4] Moissan and Charpy, *Compt. Rend.* 1895, **120**, 130.

[5] Moissan, *Compt. Rend.* 1892, **114**, 392, 617.

[6] *Annalen*, 1857, **101**, 113.

and the crucible then heated to whiteness, the boron dissolves in the molten aluminium and separates out in the crystalline form when the metal cools. The aluminium is then dissolved in caustic soda, and thus the insoluble boron is left in large transparent yellow or brownish-yellow crystals. The same modification may be obtained in smaller crystals, which are often joined together in the form of long prismatic needles, by melting together boron trioxide and aluminium. In order to prevent the action of the oxygen of the air upon the fused mass, the crucible in which the operation is conducted must be placed inside a larger one and the space between them filled up with powdered charcoal. In this process, however, the boron takes up carbon to the amount of from 2 to 4 per cent. This carbon must be in the form of diamond carbon, inasmuch as the boron crystals containing this impurity are transparent, and more transparent the larger the percentage of carbon. In addition to carbon the boron thus prepared is found to contain a certain quantity of iron and silicon from the crucible used. These impurities can be removed by treatment with hydrochloric acid, and afterwards with a mixture of nitric and hydrofluoric acids. According to the experiments of Hampe,[1] the crystals of adamantine boron contain aluminium as well as carbon; and possess a constant composition which is represented by the formula $B_{48}C_2Al_3$.

It may also be prepared by heating boric acid with aluminium turnings and sulphur, and treating the cooled mass with water, when aluminium sulphide is decomposed and crystalline boron left.[2]

In the preparation of crystalline boron the occurrence of certain graphite-like laminæ has been observed. These were at one time supposed to be a third modification of boron until Wöhler and Deville[3] showed that they consist of a compound of boron and aluminium, having the formula AlB_2.

In addition to these substances, large black plates of an aluminium boride, AlB_{12}, and smaller black crystals of carbon boride, CB_6, have been observed.[4]

According to W. H. Miller, boron crystallises in monoclinic pyramids or prisms, shown in Figs. 168 and 169, which have a lustre and a hardness exceeded only by that of the diamond, as they scratch both ruby and corundum. The specific gravity

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[1] *Annalen*, 1876, **183**, 75.

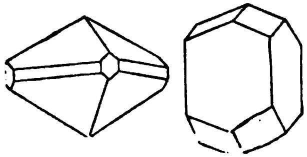
[2] Kühne, German Patent, 147871.

[3] *Annalen*, 1867, **141**, 268.

[4] Joly, *Compt. Rend.* 1883, **97**, 456.

of this form of boron is 2·68. When heated in the air or in oxygen it ignites at the same temperature as does the diamond, and then does not oxidise throughout the mass, but becomes covered with a coating of the melted trioxide (Wöhler). Concentrated nitric acid exerts no action upon it, and even aqua regia attacks it but slowly. Boiling caustic soda solution likewise does not act upon it, but if it is fused with the solid alkali it dissolves slowly with formation of sodium borate and with evolution of hydrogen.

419 *The Atomic Weight of Boron.*—The composition of borax, $Na_2B_4O_7 + 10H_2O$, has been made the basis of the determination of the atomic weight of boron by many chemists, although, owing to the volatility of boric acid and the presence of water of crystallisation in the salt, it is difficult to attain great accuracy in its analysis. By determining the water of crystallisation, Berzelius[1] obtained the number 10·98, Laurent[2] 10·84, and Ramsay and Aston[3] 10·85. The last-named chemists, moreover, obtained the number 10·89 by converting anhydrous borax into sodium chloride by distillation with methyl alcohol and hydrochloric acid, whilst Rimbach,[4] by the titration of borax with hydrochloric acid in presence of methyl orange as an indicator, found 10·86. Deville[5] analysed the chloride and bromide of boron, obtaining the numbers 10·73 and 10·88, and Abrahall[6] by the analysis of the bromide found 10·74, whilst Gautier[7] by decomposition of the chloride and bromide with water obtained the numbers 11·01 and 11·02. The number now employed is 10·9.



FIGS. 168, 169.

BORON AND HYDROGEN.

420 Davy showed that when amorphous boron is heated with potassium, and the product treated with water, a gas is evolved possessing a peculiar odour, and supposed by him to be a

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[1] *Pogg. Ann.* 1826, **8**, 19.

[2] *Compt. Rend.* 1849, **29**, 7, and *J. pr. Chem.* 1849, **47**, 415.

[3] *Journ Chem. Soc.* 1893, 207.

[4] *Ber.* 1893, **26**, 164.

[5] *Ann. Chim. Phys.* 1859, [3], **55**, 181.

[6] *Journ. Chem. Soc.* 1892, 650.

[7] *Compt. Rend.* 1899, **129**, 595.

hydride of boron. On dissolving in hydrochloric acid the mass obtained by heating iron filings and boron trioxide to whiteness, hydrogen is evolved, and this on ignition burns with a green flame. Gmelin at first supposed that this gas contained boron, but afterwards believed that its properties were due to other impurities. Deville and Wöhler doubted the existence of this hydride, and hence it was generally assumed that boron was the only non-metallic element which did not combine with hydrogen, until Francis Jones[1] succeeded in preparing the compound BH_3. He heated boron trioxide with magnesium dust in the following proportions:—

$$6Mg + B_2O_3 = 3MgO + B_2Mg_3,$$

and by the addition of hydrochloric acid to the grey friable mass so formed, which contains, in addition to magnesia and magnesium boride, boron nitride, free boron, and magnesium, obtained boron hydride mixed with so much hydrogen that its preparation in the pure state was impossible.

Ramsay and Hatfield[2] passed the gas thus obtained through a wash bottle, cooled in liquid air, where white crystals were deposited; after removal of the gases *in vacuo*, these were heated, and then melted and vaporised, giving a gas having a fœtid odour and a density of 19·36, which burnt in air with a green flame. Sparks passed through this gas decomposed it, giving boron and hydrogen, and, by estimating this boron, numbers were obtained agreeing roughly with the formula B_3H_3.

Further attempts to prepare this compound in the same manner, however, yielded a substance, which, unlike the first, was decomposed by sulphuric acid and potassium hydroxide, and possessed when vaporised a density of 18·1; Ramsay and Hatfield therefore conclude that there are two isomeric hydrides of the formula B_3H_3.

The gas prepared from the magnesium boride mixture, after removal of this hydride as above, was found to consist of a mixture of hydrogen and boron trihydride.

The trihydride is colourless, possesses an extremely unpleasant and very characteristic odour, and when inhaled, even in small quantities, produces sickness and headache. It dissolves slightly in water, and its solution does not undergo

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[1] *Journ. Chem. Soc.* 1879, 41.

[2] *Proc. Chem. Soc.* 1901, 152.

change on standing. It burns with a bright green flame, and decomposes into its constituent elements at a red heat. When it is passed into a solution of silver nitrate a black precipitate is thrown down, although only in small quantities, this being probably owing to the formation of free nitric acid. This precipitate contains boron and silver, and is decomposed by hot water with evolution of boron hydride. When this gas is passed into ammonia the peculiar smell of boron hydride disappears, but the gas has a fœtid odour, and burns with a yellow-green flame. The characteristic smell of the gas is again observed when the ammoniacal solution is acidified. An accurate analysis of the gas was not found to be possible, but the results obtained by combustion with copper oxide agree as nearly as could be expected with the formula BH_3.[1]

BORON AND THE HALOGENS.

421 *Boron Trifluoride*, BF_3.—This gas was discovered in the year 1808 by Gay-Lussac and Thénard. They obtained it by heating a mixture of one part of boron trioxide with two parts of fluor-spar to whiteness in a gun-barrel. It may be more easily prepared by heating the above mixture with twelve parts of strong sulphuric acid in a glass flask (J. Davy) :—

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O.$$

Another method is to heat a mixture of potassium boro-fluoride and the trioxide with sulphuric acid (Schiff) :—

$$6KFBF_3 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O.$$

It may also be prepared by acting on a mixture of boron nitride and sodium fluoride with sulphuric acid, when ammonium sulphate and boron fluoride are obtained.[2]

Both amorphous and crystalline boron become ignited in fluorine gas, the trifluoride being formed.[3] The colourless gas evolved by any of these processes must be collected over mercury or by displacement, as it is dissolved when brought in contact with water. It fumes strongly in the air, does

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[1] Jones and Taylor, *Journ. Chem. Soc.* 1881, 213.
[2] Moeser and Erdmann, *Ber.* 1902, **35**, 535.
[3] Moissan, *Ann. Chim. Phys.* 1891, [6], **24**, 244.

not attack glass, possesses an intensely pungent odour, and has a specific gravity of 2·37 (J. Davy). It acts upon certain organic bodies by withdrawing from them the elements of water, and carbonises them like sulphuric acid. Potassium and sodium burn very brilliantly when heated in the gas.

When equal volumes of ammonia and boron trifluoride are brought together, a compound, BF_3,NH_3, is produced. This is a white opaque solid, which can be sublimed without alteration. If one volume of the fluoride be brought in contact with two or three volumes of ammonia, the gases condense and form colourless liquids, having the composition $BF_3(NH_3)_2$ and $BF_3(NH_3)_3$. These substances lose ammonia on heating, and are converted into the solid compound (J. Davy).

Borofluoric or Hydrofluoboric Acid, HBF_4.—When fluoride of boron is brought in contact with water, boric and borofluoric acids remain in solution; thus:—

$$8BF_3 + 6H_2O = 6HBF_4 + 2B(OH)_3.$$

This acid is also formed when aqueous hydrofluoric acid is saturated with boric acid (Berzelius).

Borofluoric acid is monobasic and when brought in contact with bases a series of salts termed the borofluorides is obtained (Berzelius). The same salts are formed by bringing together the acid fluoride of an alkali with boric acid. In this case the peculiar phenomenon presents itself of solutions which, to begin with, have an acid reaction, becoming alkaline when they are mixed together. This is explained by the following equation:—

$$B(OH)_3 + 2NaHF_2 = NaBF_4 + NaOH + 2H_2O.$$

Most of the borofluorides are soluble in water, and crystalline; when heated they evolve boron trifluoride, the corresponding fluoride remaining behind.

422 *Boron Trichloride*, BCl_3.—When brought into chlorine gas amorphous boron takes fire spontaneously, with formation of boron trichloride,[1] and this same body is formed, also with the evolution of light and heat, when hydrochloric acid gas is passed over amorphous boron (Wöhler and Deville). In order to prepare boron trichloride, a current of dry chlorine gas is

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[1] Berzelius, *Pogg Ann.* 1824, **2**, 147.

passed over a strongly heated mixture of boron trioxide and charcoal:[1]—

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO.$$

For the purpose of preparing boron trichloride by this method the arrangement represented in Fig. 170 was employed. It consists of a porcelain tube, *a b*, placed in a furnace, and containing an intimate mixture of fused boric acid and charcoal. The vapour of the volatile trichloride is admitted into a Y-shaped tube, *e*, the lower limb of which is placed in a freezing mixture; this condenses the chloride, and the excess of chlorine passes away by the other limb. The temperature of the furnace must be high, as the reduction of the oxide in presence of chlorine only takes place at a bright red heat. In order to free the product from the excess of chlorine, the liquid is shaken with mercury, and the pure trichloride distilled off.

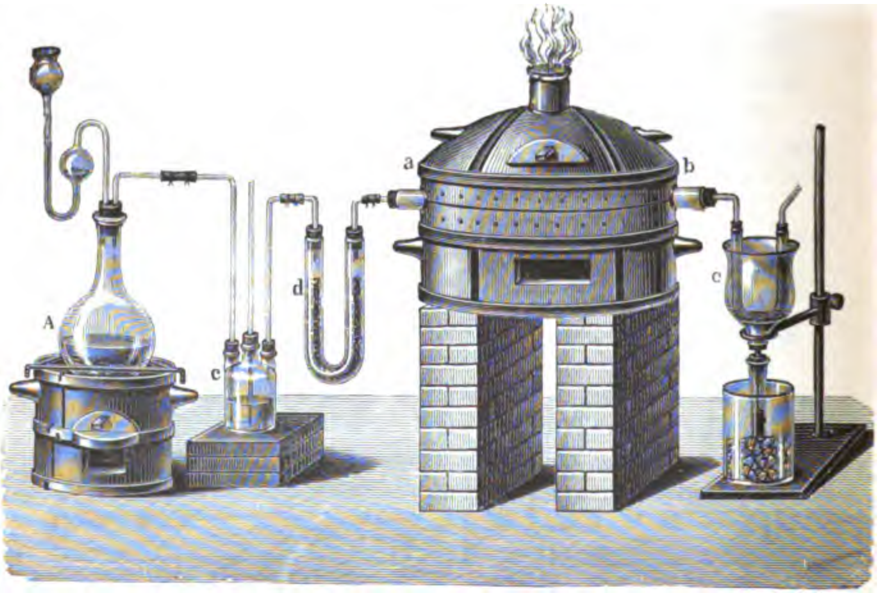

FIG. 170.

Boron trichloride is also obtained when the finely powdered trioxide is mixed with double its weight of phosphorus pentachloride, and heated in a sealed tube for three days at a tempera-

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[1] Dumas, *Ann. Chim. Phys.* 1826, [2], **31**, 436; 1826, **33**, 376.

ture of 150°. The tube is well cooled, opened, first warmed in a water-bath, and afterwards heated to redness, in order to drive off the last portions of the chloride which remain in combination with boron trioxide (Gustavson).

The chloride can also be readily obtained by passing chlorine over the crude boron obtained by heating borax with half its weight of magnesium powder.[1]

Boron trichloride is a colourless liquid, boiling at 18°·2 (Regnault). At 17° it has a specific gravity of 1·35. On heating in closed tubes it expands very rapidly, and yields a colourless vapour, which has a specific gravity of 4·065. Boron trichloride fumes strongly in the air, and is decomposed in contact with water into hydrochloric and boric acids. When brought together with small quantities of cold water it forms a solid hydrate, and this when ignited in a current of hydrogen decomposes into hydrochloric acid and amorphous boron. Boron trichloride can be distilled over sodium without undergoing decomposition, and zinc dust does not act upon it at temperatures below 200°. When the chloride and trioxide are brought together in the proportion of two molecules of the former to one of the latter, and the mixture heated in a closed tube to 150°, a white gelatinous mass is produced, from which half of the chloride is driven off at 100°, whilst the other half is not volatilised below a red heat. It would thus appear that an oxychloride is formed (Gustavson); thus:—

$$3BOCl = B_2O_3 + BCl_3.$$

When boron trichloride is heated with sulphuric anhydride in a closed tube to 120°, sulphuryl chloride is formed (Gustavson):—

$$3SO_3 + 2BCl_3 = 3SO_2Cl_2 + B_2O_3.$$

423 *Boron Tribromide*, BBr_3.—This compound can be obtained by the direct union of the two elements at a red heat, but it is best prepared by passing the vapour of bromine over a mixture of charcoal and boron trioxide and rectifying the product over mercury. It may be also obtained by passing bromine vapour over pure boron at a dull red heat and distilling the product over silver.[2] It is a colourless, strongly fuming liquid, having a specific gravity of 2·69 and boiling at 90°·5 (Wöhler and Deville). Its vapour is colourless, and has the normal specific

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[1] Gattermann, *Ber.* 1889, **22**, 195.

[2] Gautier, *Compt. Rend.* 1899, **129**, 595.

gravity of 8·78. It behaves towards water and ammonia exactly in the same way as the chloride.

424 *Boron Triiodide*, BI_3.—Pure boron does not combine directly with iodine, but the iodide may be prepared by passing boron trichloride and hydrogen iodide through a hot porcelain tube, or by passing dry hydrogen iodide over impure amorphous boron heated to the softening point of potash glass. It forms white crystalline plates, melts at 43°, boils at 210°, is very hygroscopic, and is decomposed by water in a similar manner to the chloride. It dissolves in carbon bisulphide, benzene, &c., and has a density of 3·3 at 50°. It very readily parts with its iodine in chemical reactions, and has therefore been used in the preparation of iodine derivatives of other elements.[1]

OXIDES AND OXY-ACIDS OF BORON.

BORON TRIOXIDE, B_2O_3, AND BORIC OR BORACIC ACID, H_3BO_3.

425 Boron trioxide, the only known oxide of the element, is obtained when boron burns in the air, or in oxygen. It is, however, best prepared by heating boric acid to redness; thus:—

$$2B(OH)_3 = B_2O_3 + 3H_2O.$$

The fused mass thus obtained solidifies to a brittle glassy solid, having a specific gravity at 4° of 1·83. It is a very hygroscopic substance, uniting easily with water to form boric acid. It is not volatile at a red heat, but volatilises when heated to whiteness. In consequence of its non-volatility, boron trioxide decomposes, at a red heat, all salts whose acids or corresponding oxides are volatile at a lower temperature, and thus carbonates, nitrates, sulphates, and other salts are converted into borates. Most metallic oxides dissolve in fused boron trioxide at a red heat, many of them imparting to the mass characteristic colours; hence this substance is much used in blowpipe analysis.

Orthoboric Acid, $B(OH)_3$.—This compound is formed by the union of the oxide with water. It was first prepared by the decomposition of borax by means of a mineral acid, and known under the name of Homberg's *sal sedativum*. In the year 1774, Höfer, a Florentine apothecary, observed the occurrence

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[1] Moissan, *Compt. Rend.* 1891, **112**, 717; 1892, **114**, 617.

of this compound in the water of the lagoons of Monte Rotondo in Tuscany, and in 1815 a manufactory was erected on the spot for the purpose of obtaining boric acid from the water. The undertaking did not flourish until the year 1828, owing to the cost of fuel needed for the evaporation of the water containing the acid in solution. In that year Larderel gave a new impetus to the manufacture by using the natural heat of the volcanic jets of steam, termed *suffioni*, to evaporate the water charged with the acid.

Almost the whole of the boric acid brought into the European market is derived from these Tuscan lagoons. Large volumes of steam issue from volcanic vents near Monte Rotondo, Lago Zolforeo, Sasso, and Larderello, and this steam is condensed in the lagoons. The vapours themselves, the temperature of which varies between 90° and 120°, contain only traces of boric acid, but when this steam is allowed to pass into the lagoons the water soon becomes charged with the substance, and on evaporation yields crystals of the acid. During the last fifty years many borings have been made through the eocene strata, and thus artificial suffioni have been formed.

In order to obtain the boric acid the suffioni are surrounded by basins, built of bricks or of glazed masonry, large enough to contain two or three of the vents. Several of these basins are usually built on the side of a hill, as shown in Fig. 171, and the water of a spring or lagoon is allowed to run into the uppermost one. The steam and gases are then permitted to pass through this water for twenty-four hours, after which it is conducted by a wooden pipe to the second basin, and so on until the liquor has passed through from six to eight basins and cannot take up any more boric acid. It then contains about 2 per cent. of this substance. After settling, the clear liquid is run in a thin stream on to a large sheet of corrugated lead, 125 metres in length and 2 metres in breadth, placed in a slightly inclined position and kept hot by the vapours from the suffioni, which are allowed to pass underneath. In this way 20,000 litres of water can be evaporated every twenty-four hours. The liquid running off the end of the plate is then further evaporated in leaden pans until the boric acid begins to crystallise out.

Hot water flows out from some of the artificial suffioni, and this sometimes contains as much as 0·4 per cent. of boric acid, and may be directly brought on to the pan. The

FIG. 171.

water of the Lago Zolforeo formerly contained only 0·05 per cent. of boric acid, but this percentage has been considerably raised by cutting off all ingress of fresh water, and damming off that part of the lake to which the suffioni have access. The temperature in this portion of the lake was thus raised to 65°, and the water contained from 0·2 to 0·3 per cent. of the acid, whilst in the other portion the water had a temperature of 26° and only contained 0·08 per cent. of boric acid. These lagoons produce no less than from 1,200 to 1,500 kilos. of boric acid daily. In order to purify the commercial acid, which contains about 25 per cent. of foreign matter, it is recrystallised from hot water and then dried in chambers heated by the suffioni.

It is still a matter of doubt in what form the boric acid, thus obtained, occurs in the earth. The occurrence of ammoniacal salts and sulphide of ammonium, together with the boric acid, is very remarkable. The most probable hypothesis appears to be that of Wöhler and Deville,[1] according to which the acid is derived from the decomposition of a nitride of boron, BN. Boron is one of the elements which can combine directly with nitrogen, and the compound thus formed is decomposed by steam into boric acid and ammonia.[2]

This theory is rendered the more probable by the observation made by Warrington, that the boric acid and sal-ammoniac found in the crater of the Island of Volcano contain traces of boron nitride.[3] It is, however, possible that boric acid may be derived from a sulphide of boron, which is decomposed by water into sulphuretted hydrogen and boric acid (Sartorius von Waltershausen).

Boric acid is also manufactured from certain minerals, such as borocalcite, which occurs in considerable quantities in the nitre beds of Peru and Chili. It is likewise prepared from the natural borax or tincal, which was first obtained from the basins of dried-up lagoons in Central Asia, and has been found in the borax lake in California in such quantities that the amount there obtained is sufficient to supply the whole demand of the United States. For the purpose of preparing boric acid from these sources, the minerals are dissolved in hot hydrochloric acid, the boric acid, which separates out on cooling, being recrystallised from hot water.

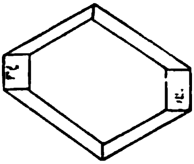

FIG. 172.

Boric acid crystallises from aqueous solution in shining six-sided laminæ unctuous to the touch, and belonging to the triclinic system, having the form shown in Fig. 172. It has a specific gravity of 1·4347 at 15° (Stolba), and is much more

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[1] *Annalen*, 1850, **74**, 72; 1858, **105**, 71.

[2] Compare Popp, "Ueber die Bildungsweise der Borsäure in den Fumerolen Toscanas." *Annalen*, Suppl. 1872, **8**, 5.

[3] *Chemical Gazette*, 1855, 419.

readily soluble in hot than in cold water, as is shown by the following table (Brandes and Firnhaber):—

	Parts of water.	At
One part of boric acid requires for solution	25·66	19°
,, ,, ,,	14·88	25°
,, ,, ,,	12·66	37°·5
,, ,, ,,	10·16	50°
,, ,, ,,	6·12	62°·5
,, ,, ,,	4·73	75°
,, ,, ,,	3·55	87°·5
,, ,, ,,	2·97	100°

Boric acid is a weak acid, and its cold saturated solution colours blue litmus tincture of a wine-red colour like carbonic acid, but is without action on methyl-orange. When the solution is boiled, the acid volatilises with the aqueous vapour, and this property explains the presence of the acid in the suffioni. Boric acid is also easily soluble in alcohol, and when this solution is inflamed it burns with a characteristic green-edged flame. The same green tint is seen when a small bead of the molten acid on the end of a very fine platinum wire is brought into the fusion-zone of a non-luminous flame. The spectrum of this green flame consists of several bright bands: the brightest of these (α) is situated in the yellowish green, and two others (β and γ), equally characteristic, occur in the green.[1]

The action of boric acid upon the colouring matter of turmeric is highly characteristic. If a piece of paper coloured with turmeric be moistened with a solution of the acid to which a little hydrochloric acid has been added, and the paper dried, it turns pink, which further changes to blue or green on the addition of dilute alkali. Ordinary indicators cannot be used for the titration of boric acid with caustic soda; thus, with phenol phthalein a red coloration is produced before all the boric acid has been changed into sodium borate. If, however, phenol phthalein be used in the presence of excess of glycerin, the boric acid may be then estimated by titration with standard caustic soda solution, the reaction taking place according to the equation:[2]—

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$$

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[1] Lecoq de Boisbaudran, *Spectres Lumineux*, 193.

[2] Hönig and Spitz, *Zeit. angew. Chem.* 1896, 549.

When boric acid is heated with methyl alcohol it volatilises, and may be estimated in this way by distilling it into a weighed quantity of lime, magnesia or sodium tungstate, evaporating to dryness and determining the increase of weight.[1]

Metaboric Acid, $BO(OH)$, is produced when boric acid is heated to 100°. It forms a white powder, which at the above temperature undergoes a slow but complete volatilisation.[2]

Pyroboric Acid, $B_4O_5(OH)_2$.—This substance is a brittle glass-like mass, obtained when boric acid is heated for a long time to 140°.

Boric acid dissolves readily in fuming sulphuric acid, and from this solution tabular crystals separate out, having the composition :—

$$2SO_4\left\{\begin{matrix}H\\OB\end{matrix}\right.+SO_3.$$

These crystals when heated evolve sulphur trioxide.

When boric acid is evaporated with an excess of concentrated phosphoric acid, and the dry residue treated with water in order to separate the phosphoric acid, a white amorphous mass is left, which possesses the composition BPO_4. This substance is infusible, it is not attacked by strong acids, but dissolves in aqueous potash. The existence of these compounds points to the conclusion that boron trioxide possesses feebly basic properties, resembling, in this respect, alumina, Al_2O_3, which also sometimes acts as a weak acid, and sometimes as a weak base, forming a corresponding phosphate, $AlPO_4$.

426 *The Borates.*—Boric acid, like phosphoric acid, forms many series of salts, several of which are derived from the above-named modifications of the acid. Orthoboric acid is tribasic; but its salts are very unstable, and the only well-defined orthoborate which is known is $Mg_3(BO_3)_2$. The tribasic character of boric acid is, however, clearly shown by its volatile ethereal salts, compounds in which the hydrogen of the boric acid is replaced by the organic radical, C_2H_5. Thus ethyl orthoborate, $B(OC_2H_5)_3$, is a colourless liquid, which volatilises without decomposition, and has a vapour density corresponding to the above formula.

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[1] Gooch and Jones, *Zeit. anorg. Chem.* 1899, **19**, 417.

[2] Schaffgotsch, *Pogg. Ann.* 1859, **107**, 427.

The metaborates are much more stable compounds. Thus we are acquainted with the following:—

Potassium metaborate	KBO_2.
Sodium metaborate	$NaBO_2$.
Magnesium metaborate	$Mg(BO_2)_2$.
Calcium metaborate	$Ca(BO_2)_2$.

The pyroborates are also stable compounds, and to this class belong the following:—

Borax, or sodium pyroborate . . .	$Na_2B_4O_7$.
Borocalcite, or calcium pyroborate .	CaB_4O_7.
Boronatrocalcite (ulexite)	$Na_2B_4O_7+2CaB_4O_7$.

In addition to these, other salts are known which have a more complicated constitution, corresponding in this respect to certain classes of phosphates. The following are examples of such borates:—

Larderellite	$(NH_4)_2B_8O_{13}$.
Lagonite	$Fe_2B_6O_{12}$.
Boracite	$2Mg_3B_8O_5+MgCl_2$.

The crystalline borates almost always contain water of crystallisation, and, with the exception of those of the alkalis, are either insoluble or only slightly soluble in water. They are all easily decomposed by acids, and therefore, when they are warmed with sulphuric acid and alcohol, and the mixture is ignited, the characteristic green flame of boric acid is observed. The same green coloration is observed when a trace of a borate is brought on to a platinum wire with a small quantity of acid potassium sulphate, and this held in the non-luminous flame. Boric acid is a mild antiseptic, and both the free acid and borax are used as preservatives for milk, butter, and similar articles.

Perboric Acid.—By the action of hydrogen peroxide on aqueous solutions of orthoborates, or by the electrolysis of such solutions, bodies which possess the power of liberating iodine from potassium iodide and of decolorising potassium permanganate are stated to be formed, and these have been called perborates;[1] thus sodium perborate is stated to possess the formula $NaBO_3+4H_2O$.

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[1] Tanatar, *Zeit. physikal. Chem.* 1898, **26**, 132; and *Zeit. anorg. Chem.* 1901, **26**, 343. Constam and Bennett, *Zeit. anorg. Chem.* 1900, **25**, 265; 1901, **26**, 451.

427 Boric acid and the borates form double compounds with fluorides, and these bodies have been called fluoborates or fluoroborates.

By dissolving boric acid in aqueous hydrofluoric acid and evaporating, a liquid of the composition $H_2B_2O_4,6HF$ or $BF_3 + 2H_2O$ is left. This substance is also formed when boron fluoride is passed into water, and the mixture of boric and borofluoric acids so formed evaporated. This liquid boils between 165° and 200°, and undergoes partial decomposition, boric acid being formed, whilst the specific gravity of the vapour shows that it is wholly dissociated in the gaseous state.[1]

By neutralising the liquid with alkalis, salts of the composition $M_2B_2O_4,6MF + H_2O$ have been obtained (Berzelius), and the sodium compound may also be prepared by crystallising a mixture of sodium fluoride and sodium borate. The existence of this acid is, however, doubtful, and it may consist of a solution of boric acid in borofluoric acid, whilst the last-mentioned salts are probably mixtures of fluorides and borates (Basarow). Other fluoborates that have been described are $2KF,B_2O_3$ and $BF(OK)_2$.

By the action of hydrogen peroxide upon fluoborates, fluoperborates are stated to be formed.[2]

Chloroborates and bromoborates of the general formula $6M''O,8B_2O_3,M''X_2$, where M'' represents a dyad metal and X the halogen, have also been described.[3]

BORON AND SULPHUR.

428 *Boron Trisulphide*, B_2S_3.—Berzelius first obtained this compound by heating boron in the vapour of sulphur. It can be most readily prepared by the action of the vapour of carbon bisulphide upon an intimate mixture of lamp-black and boron trioxide (Wöhler and Deville):—

$$3CS_2 + 3C + 2B_2O_3 = 2B_2S_3 + 6CO.$$

It may also be obtained[4] by heating boron to bright redness

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[1] Basarow, *Ber.* 1874, **7**, 824, 1121.

[2] Melikoff and Lordkipanidze, *Ber.* 1899, **32**, 3349, 3510; Petrenko, *J. Russ. Phys. Chem. Soc.* 1902, **34**, 37.

[3] Rousseau and Allaire, *Compt. Rend.* 1895, **118**, 1255; 1895, **119**, 71.

[4] Sabatier, *Compt. Rend.* 1891, **112**, 862; Moissan, *Compt. Rend.* 1892, **115**, 203.

in a current of sulphuretted hydrogen, or by heating boron iodide with sulphur above 440°.

Boron trisulphide occurs generally as a white, glassy, fusible solid, but it is sometimes obtained in the form of silky needles. It melts on heating, softening at 310°, has a density of 1·55, and can be distilled in a current of sulphuretted hydrogen. It is at once decomposed in contact with water, with formation of boric acid and sulphuretted hydrogen:—

$$B_2S_3 + 6H_2O = 2B(OH)_3 + 3H_2S.$$

It possesses a pungent smell and attacks the eyes.

If a hot solution of boron tribromide in carbon bisulphide or benzene be saturated with sulphuretted hydrogen, long white needles of *metathioboric acid* crystallise out on cooling. This substance has the composition B_2S_3,H_2S, and on heating above 100° splits up into sulphuretted hydrogen and boron trisulphide.[1]

It is decomposed by water giving boric acid and hydrogen sulphide, and dissolves in liquid ammonia yielding yellow crystals of the composition $B_2S_3,6NH_3$, when the excess of ammonia is evaporated off at ordinary temperatures.[2]

Boron Pentasulphide, B_2S_5.—This compound is formed as a white crystalline powder by treating a solution of sulphur in carbon bisulphide at 60° with boron iodide. It melts at 390°, has a density of 1·85, and is decomposed by water into sulphuretted hydrogen, sulphur, and boric acid.[3]

BORON AND NITROGEN.

Boron Nitride, BN.

429 Amorphous boron combines directly with nitrogen at a white heat to form the above compound, which is also produced when the compound of chloride of boron and ammonia is passed, together with ammonia gas, through a red-hot tube (Martius). Boron nitride was first obtained by Balmain, in the year 1842, by heating boron trioxide with the cyanide of potassium or of mercury:—

$$B_2O_3 + Hg(CN)_2 = 2BN + CO + CO_2 + Hg.$$

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[1] Stock and Poppenberg, *Ber.* 1901, **34**, 399.

[2] Stock and Blix, *Ber.* 1901, **34**, 3039.

[3] Moissan, *Compt. Rend.* 1892, **115**, 271.

The best mode of preparing the substance is by heating an intimate mixture of one part of anhydrous borax with two parts of dry sal-ammoniac to redness in a platinum crucible (Wöhler). The mass is washed first with water containing hydrochloric acid, and afterwards with pure water, and, lastly, treated with hydrochloric acid in order to remove completely the boric acid which is mixed with the nitride. The reaction which takes place is represented by the equation:—

$$Na_2B_4O_7 + 4NH_4Cl = 4BN + 2NaCl + 2HCl + 7H_2O.$$

It may also be obtained by passing ammonia over a strongly heated and previously fused mixture of boron trioxide and tricalcium phosphate, and purifying the product by washing with dilute hydrochloric acid.[1]

The nitride thus obtained is a white, light, perfectly amorphous powder, resembling finely-divided talc. When it is heated in the flame it phosphoresces with a bright greenish-white light. Heated in a current of steam it yields ammonia and boric acid:—

$$BN + 3H_2O = H_3BO_3 + NH_3.$$

Hydrofluoric acid dissolves the nitride slowly with formation of ammonium borofluoride, thus:—

$$BN + 4HF = NH_4BF_4.$$

Boron nitride reduces many metallic oxides on being fused with them, giving the metal, borates and nitrous oxide; sulphates are reduced to sulphides, whilst carbon dioxide and sulphur dioxide are partially reduced when heated with the nitride (Moeser and Erdmann).

430 *Boramide*, $B(NH_2)_3$, *and Borimide*, $B_2(NH)_3$.—Boramide has been obtained by passing a current of hydrogen, carrying with it boron trichloride, through liquid ammonia at a temperature of $-50°$ to $-70°$, the excess of ammonia being volatilised first at $-23°$ and finally at 0°, when the white solid boramide and ammonium chloride are left. The reaction takes place thus:—

$$BCl_3 + 6NH_3 = 3NH_4Cl + B(NH_2)_3.$$

It has not yet been found possible to separate the boramide completely from ammonium chloride.

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[1] Moeser and Erdmann, *Ber.* 1902, **35**, 535.

It is decomposed by water, giving ammonium borate, and loses ammonia slowly at ordinary temperatures, and rapidly at 440°, giving borimide,[1] thus:—

$$2B(NH_2)_3 = B_2(NH)_3 + 3NH_3.$$

Borimide may also be prepared by heating the additive compound $B_2S_3,6NH_3$ (p. 718) to 115—120° in a stream of ammonia, when it decomposes, giving borimide and sulphur, the latter being removed by continued heating in ammonia.[2]

It is a white powder, decomposed by water with evolution of heat, yielding ammonium borate, and, on heating, yields boron nitride and ammonia.

When shaken with liquid hydrogen chloride it forms a white hydrochloride, $B_2(NH)_3,3HCl$.

BORON AND PHOSPHORUS.

431 Boron does not combine directly with phosphorus, but a phosphide can be prepared by the use of boron iodide.[3] When this substance and yellow phosphorus are dissolved in carbon bisulphide, a red insoluble powder is formed, which can be sublimed *in vacuo* at 200° in red crystals. This compound has the formula PBI_2, is very hygroscopic, and is decomposed by water. When it is heated at 160° in hydrogen it loses one atom of iodine, forming a volatile crystalline substance of the formula PBI; which on further heating in hydrogen is converted into boron phosphide, PB. This compound is a colourless insoluble powder, which burns brilliantly in the air at 200°, and on strong ignition in a current of hydrogen is converted into a lower phosphide of the formula P_3B_5. Phosphide of boron is also formed when the white solid compound of boron bromide with phosphine, BBr_3PH_3, is heated at 300°, hydrobromic acid being evolved.[4]

Boron tribromide combines with phosphorus trichloride at ordinary temperatures, forming colourless crystals of $PCl_3,2BBr_3$, melting at 58°, and with phosphorus pentachloride in sealed

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[1] Joannis, *Compt. Rend.* 1900, **135**, 1106.

[2] Stock and Blix, *Ber.* 1901, **34**, 3039.

[3] Moissan, *Compt. Rend.* 1891, **113**, 624, 726.

[4] Besson, *Compt. Rend.* 1891, **113**, 78.

tubes at 150°, giving colourless crystals of $PCl_5.2BBr_3$, whilst the compound, $P_2I_4 2BBr_3$, has been obtained by adding boron bromide to a solution of phosphorus diiodide in carbon bisulphide.

These compounds are all decomposed by water yielding phosphorus and boric acids, together with hydrobromic and hydrochloric or hydriodic acids.[1]

CARBON. C = 11·91. (H = 1).
= 12·00. (O = 16).

432 Carbon occurs in the free state in nature in two distinct allotropic crystalline modifications as *diamond* and *graphite.* It forms, moreover, an invariable constituent of all organised bodies, and when any such substance is heated in absence of air, a portion of the carbon remains behind in the third form of *amorphous* carbon or charcoal.

Diamond.—On account of its brilliant lustre and remarkable hardness the diamond has been valued for ages as a precious stone. Manilius appears to be the first to mention it in his *Astronomia:* "Adamas punctum lapidis, pretiosior auro." Up to the year 1777 the diamond was believed to be a species of rock-crystal, but Bergman in that year proved, by means of blowpipe experiments, that the diamond contained no silica, and came to the conclusion that it was composed of a peculiar earth to which he gave the name of *terra nobilis.* But as soon as the fact of its combustibility had been definitely ascertained it was classed amongst the fossil resins.

This combustibility of the diamond appears to have been observed at an early period, although the fact does not seem to have attracted the general attention of the older chemists, as statements of a contrary character are recorded by them. Thus, for instance, Kunkel states that his father, at the command of Duke Frederick of Holstein, heated diamonds in his gold-melting furnace, for nearly thirty weeks, without their undergoing any change. It is to Newton, however, that we owe the first argument which went to prove that the diamond was capable of undergoing combustion on account of its high refractive power, a property characteristic of the class of oily bodies. In the second book of his *Opticks*, Newton says upon

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[1] Tarible, *Compt. Rend.* 1901, **132**, 83.

the subject, "Again the refraction of camphire, oyl-olive, lintseed oyl, spirit of turpentine and amber, which are fat sulphureous unctuous bodies, and a diamond, which probably is an unctuous substance coagulated, have their refractive powers in proportion to one another as their densities without any considerable variation." The conclusion to which Newton was led by theoretical considerations was experimentally proved to be correct in the year 1694–5 by Averami and Targioni, members of the Academia del Cimento, who, at the request of the Grand Duke Cosmo III., of Tuscany, placed a diamond in the focus of a large burning-glass and observed that it entirely disappeared. Francis I., who is said to have received from an alchemist an anonymous receipt for melting diamonds, exposed, in the year 1751, diamonds and rubies of the value of 6,000 gulden for twenty-four hours to the action of a powerful fire; the rubies were found unaltered, but the diamonds had altogether disappeared. The volatilisation of the diamond by means of heat was from this time forward made the subject of numerous experiments. Thus, Darcet observed in 1766 that diamonds disappear when they are heated in a cupel-furnace, even in closed crucibles, but, continuing his experiments at the request of the Paris Academy, he, together with Rouelle, found that when heated in perfectly hermetically-sealed vessels, the diamond did not disappear. Macquer, in the year 1771, was the first to observe that when the diamond undergoes volatilisation it appears to be surrounded by a flame. In conjunction with Cadet and Lavoisier, he afterwards found that a true combustion takes place. In continuation of these experiments Lavoisier, together with Macquer, Cadet, Brisson, and Baumé,[1] placed a diamond in a glass vessel containing air collected over mercury, and on igniting the diamond by means of a burning-glass, they found that carbonic acid gas was produced.

Charcoal and diamond were from this time forward classed together under the head of carbon, and their chemical identity was fully proved. Smithson Tennant, in 1796, corroborated these results by showing that equal weights of these two substances yielded equal weights of carbon dioxide on burning, whilst Mackenzie in 1800 added to this the proof that the same weight of graphite also gives the same weight of carbon dioxide. Allen and Pepys, in 1807, came to the same con-

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[1] Lavoisier, *Œuvres*, tome ii. 38, 64.

clusion, and Davy, from experiments made upon diamonds with the same lens which the Florentine Academicians had used in 1694, showed, in 1814,[1] that no trace of water is formed in the combustion of diamonds, thus proving that this substance contains no hydrogen, but consists of chemically pure carbon. Davy likewise reduced the calcium carbonate obtained from the air in which a diamond had burnt, by means of potassium, in this way preparing a black powder which, like ordinary carbon, took fire when thrown into a flame.

433 The diamond came to Europe from the East. The mines in Purteal, which in former days were famous as those of Golconda, and where the Koh-i-noor was found, are at present almost entirely exhausted. The diamond fields of Minas Geraes in Brazil, which have been worked since the year 1727, are probably the richest in the world and yielded yearly about 2,000 kilogr. of "stones." Of late years the diamond fields in the Cape have become celebrated, and they, together with the newly opened mines in the Transvaal, now supply nearly the whole demand of the world. In 1902 the total value of exported diamonds from South Africa was £5,427,360. Diamonds are also found in Borneo, in the Ural, in New South Wales, in Bahia, in California, in Georgia, as well as in other localities.

The substance termed *carbonado* is a porous and massive form of impure diamond, and occurs in black or brownish fragments, which, when examined with a lens, exhibit cavities filled with small octahedra. The largest specimen known, which was found in Bahia, Brazil, weighed 630 grams.[2]

The diamond always occurs in alluvial deposits in the neighbourhood of a certain kind of micaceous rock which was first observed in the Brazils, and has been termed *itacolumite.* This rock is distinguished by the fact that in thin plates or bars it is very flexible. It was for a long time doubtful whether the diamonds occur *in situ* in the rock; small diamonds have, however, been found embedded in the matrix, and Jeremejew[3] has observed the existence of microscopic diamonds in a talcose schist occurring in the Southern Ural. This rock contains a hydrated silicate termed *xanthophyllite* occurring in yellow

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[1] "Some Experiments on the Combustion of the Diamond and other Carbonaceous Substances," *Phil. Trans.* 1814, p. 557. Read June 23, 1814.

[2] Moissan, *Compt. Rend.* 1895, **121**, 449.

[3] *Ber.* 1871, **4**, 903.

tabular crystals, in the inside of which the small crystals of diamond are embedded in a direction parallel to the cleavage of the xanthophyllite.

The "blue earth" in which the diamonds occur at the Cape contains, in addition to the occasional diamonds large enough to be picked out, about 0·1–0·5 grams of crystallised carbon per cubic metre, and this can be isolated from the whole mass by first of all boiling with sulphuric acid, washing with water, and treating with aqua regia, after which the mass is again washed with water and then treated successively with hydrofluoric acid, sulphuric acid, and water twelve or fourteen times to remove the whole of the mineral matter, the residue, which amounts to about 0·094 mgr. from 2 kilogr. of earth, then consisting almost entirely of graphite, carbonado, and microscopic transparent diamonds, the graphite being present in greater proportion than the diamond.[1]

All diamonds when burnt leave a residue consisting of a small quantity of incombustible ash, those which are colourless leaving the least. The ash amounts to from 0·05–0·2 per cent. in the case of diamond, and to as much as 4·5 per cent. in the case of carbonado. It has a reddish colour, and always contains iron and silica, which are usually accompanied by lime and magnesia.[2]

Diamond has also been found, both in the form of colourless crystals and of carbonado, accompanied by graphite, in a meteorite found in Canon Diablo,[3] and this occurrence is of the highest importance, as showing that the diamond has been probably formed by crystallisation from a mass of iron heated to a high temperature.

This probability has been converted into a certainty by Moissan, who has succeeded in preparing both diamond and carbonado artificially. He has found that when carbon is allowed to crystallise from solution in molten iron or silver under a high pressure diamond is produced, whilst under ordinary conditions the carbon separates out as graphite.

In order to obtain artificial diamond, pure sugar charcoal is strongly compressed in a cylinder of soft iron, which is then

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[1] Couttolenc; Moissan, *Compt. Rend.* 1893, **116**, 292

[2] Roscoe, *Proc. Manchester Lit. and Phil. Soc*; Moissan, *Compt. Rend.* 1893, **116**, 458.

[3] Friedel, *Compt. Rend.* 1893, **116**, 290; Moissan, *Compt. Rend.* 1893, **116**, 288.

closed by a plug of the same metal. This is placed in a crucible containing about 200 grams of molten iron, melted by means of an electric furnace, and the crucible at once withdrawn from the furnace and cooled as rapidly as possible. Water does not cool the mass quickly enough, owing to the formation of a badly conducting layer of steam, and it is, therefore, better to cool the crucible by immersion in molten lead. Iron, like water, expands when it solidifies, and the solid crust first formed on the outside of the mass therefore exerts an enormous pressure on the interior portion during the crystallisation of the latter. The mass is treated with hydrochloric acid, which dissolves the iron, and the residue is then subjected to a treatment resembling that employed in isolating the crystallised carbon from the blue earth. The residue consists of graphite, a maroon-coloured variety of carbon, carbonado, and transparent colourless diamond. The densest part of this is isolated by further treatment with hydrofluoric and sulphuric acids, followed by the action of fuming nitric acid and potassium chlorate, to remove the graphite, after which the remaining fragments are separated according to their density by placing them in liquids of different densities. In this way small fragments having the crystalline form, density, and hardness of diamonds are obtained, and these are found on combustion to yield the expected amount of carbonic acid. Enlarged sketches of some of the artificial diamonds are shown in Fig 173, which exhibits their crystalline structure and octahedral shape. The size and transparency of the diamonds produced depends largely upon the rapidity of the cooling, diamonds of 0·5 mm. diameter and of the brilliant limpidity of the natural diamond

FIG. 173.

having been obtained by the use of molten lead, whilst in the fusions which were cooled by water the diamonds were much smaller and less limpid.

One of the crystals thus produced showed the interesting property, which has been observed in certain Cape diamonds, of splitting into fragments when preserved, owing probably to a state of strain produced by the rapid cooling.[1]

The diamond crystallises in hemihedral forms belonging to the regular system, the crystals being usually octahedral in type, although the simple form consisting of the two tetrahedra equally developed rarely occurs alone. Combinations of two tetrahedra, two rhombic dodecahedra, the hexakistetrahedron (*a*), or combinations (*b* and *c*) and twins (*d*) of this form as well as combinations of the hexakistetrahedron with two tetrahedra (*e*), are those which usually occur (Fig. 174). The faces of the crystals are not unfrequently curved, and the form of the crystal distorted, whilst twin crystals are also found. All diamonds cleave easily in directions parallel to the faces of the regular tetrahedron, showing this to be the primary

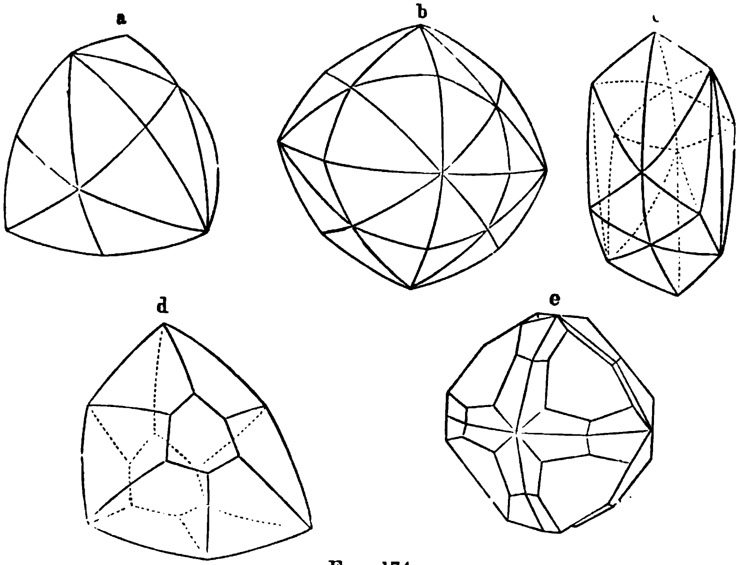

FIG. 174.

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[1] Moissan, *Compt. Rend.* 1893, **116**, 218; 1894, **118**, 320; 1896, **123**, 206, 210; see also Friedel, *Compt. Rend.* 1893, **116**, 224; Rousseau, *Compt. Rend.* 1893, **117**, 164; Rossel, *Compt. Rend.* 1896, **123**, 113; Ludwig, *Zeit. Electrochem.* 1902, **8**, 273; Hasslinger, *Monatsh.* 1902. **23**, 817.

form. The fracture is conchoidal. The crystals are usually colourless and transparent, though sometimes they are green, brown, and yellow. Blue and black crystals rarely occur. The specific gravity of diamond varies from 3·5 to 3·6, that of the purest specimens being, according to Baumhauer, 3·518 at 4°, whilst carbonado is found to vary in density from 3 to 3·5. The diamond possesses a peculiar and characteristic lustre, and refracts light very powerfully, its index of refraction being 2·417. It is also the hardest of known substances. The lustre (termed adamantine) of the diamond is greatly increased by cutting and polishing and by giving the stone numerous facets which render it capable of reflecting and dispersing light in all directions. Its remarkable lustre depends on the fact that all light which falls on an internal surface at an angle of incidence greater than 24° 13′ is totally reflected, whilst the brilliant colours of the refracted light are due to the high dispersion of the gem, which is greater than that of all other precious stones. Diamonds are cut or polished by pressing the surface of the gem against a revolving metal wheel covered with a mixture of diamond dust and oil, no other substance except boride, and perhaps silicide of carbon, being hard enough to abrade the diamond.

Most diamonds when examined under the microscope exhibit cloud-like darker portions. Dark spots are also frequently seen in them, which Brewster considered to be cavities, but Sorby has shown that they consist of small crystals of much lower refractive power than the diamond itself. The black substance often found enclosed in Brazil diamonds is according to Moissan, a different modification, as it may be burned away in a current of oxygen at temperatures 200° below that at which diamond commences to oxidise.[1]

Crystals have been found within which impressions of other diamonds are seen. Kenngott observed a yellow octahedron which was enclosed in a colourless diamond, whilst Goeppert has noticed in certain diamonds the occurrence of a cell-like structure resembling that obtained when a jelly undergoes solidification.

The specific heat of diamond at ordinary temperatures is 0·1469 (Regnault), whilst at 985° it is 0·459 (Weber).

434 The diamond burns with tolerable ease when heated in the air or in oxygen. The formation of carbon dioxide com-

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[1] *Compt. Rend.* 1896, **123**, 210.

mences in the latter gas at 720°, and is abundant at 790°, the diamond becoming incandescent and surrounded by flame at 800°.[1] If a diamond is placed on a piece of platinum foil it may be ignited by the flame of the mouth blowpipe. To demonstrate the combustibility of the diamond in oxygen and the production of carbonic acid, the apparatus shown in Fig. 175 may be employed. Two thick copper wires (*c*) pass through the caoutchouc cork fitting into the cylinder containing oxygen. These are connected together by a spiral of thin platinum wire (*b b*) wrapped round the copper. Into this spiral a splinter or small diamond (*a*) is placed, and on allowing a current from 6 to 8 Grove's cells to pass through the platinum it is heated to whiteness. The diamond then takes fire, and on breaking the circuit it is seen to burn brilliantly until it is completely consumed. A small quantity of clear lime-water may be poured into the cylinder before the experiment, and this liquid remains clear until after the diamond is burnt.

FIG. 175.

The exact identity of the gas produced by burning the diamond in oxygen with carbon dioxide has been proved by combining it with caustic soda. The resulting substance was found to be in every respect identical with ordinary sodium

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[1] Moissan, *Compt. Rend.* 1902, **135**, 921.

carbonate.[1] The spectrum given by the gas is also identical with that given by carbon dioxide prepared in the usual manner.[2]

When ignited in hydrogen, diamond undergoes no change even when heated to whiteness, and a crystal which was heated embedded in charcoal powder to the melting point of cast iron remained unchanged, while a cut brilliant, on the other hand, when thus heated became black, owing to a thin coating of graphite being formed on its surface.[3] When the diamond is heated between carbon poles by a powerful electric current it swells up and becomes converted into a black mass of graphite, and a similar change occurs on the surface when diamonds are subjected to an electric discharge of high tension in vacuo.[4]

The diamond is by no means easily attacked by most chemical reagents. It is unaffected by chlorine or hydrochloric acid at 1200°, and is not acted on when heated with potassium chlorate or iodic acid. It is moreover not attacked by boiling sulphuric acid, hydrofluoric acid, or a mixture of nitric acid and potassium chlorate, and these reagents are therefore used, as already described, for separating the diamond from the other forms of carbon and all mineral substances. When fused with sodium or potassium carbonate the diamond gradually disappears, being converted into pure carbon monoxide. The diamond is also attacked by sulphur at 1000°.[5]

The diamond is the most valuable of gems, those which are colourless and have the purest water being especially prized. The most beautiful of this kind is the Pitt or Regent diamond, which weighs 136·25 carats[6] or 431 grains, and is worth £125,000. More rarely some of the transparent but coloured "stones" are highly prized. Thus the celebrated blue Hope diamond, weighing only 4½ carats, but of peculiar beauty and brilliancy, is valued at £25,000.

Among other celebrated diamonds, that in the possession of the Nizam of Hyderabad must be mentioned. It was found about half a century ago, having been used by a child as a toy.

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[1] Krause, *Ber.* 1890, **23**, 2409.

[2] Roscoe and Schuster, *Proc. Manchester Lit. and Phil. Soc.* **7**, 80.

[3] G. Rose, *Berlin Acad. Ber.* 1872, p. 516.

[4] Crookes, *Chem. News*, 1896, **74**, 39.

[5] Moissan, *Compt. Rend.* 1893, **116**, 460.

[6] The word "carat" (Arabic, "qîrat") is derived from κεράτιον, St. John's bread, or karob, the seeds of this plant having been formerly used as weights. 1 diamond carat = 3·17 grains or 0·2054 grm.

During the Indian mutiny a portion of this diamond was broken off, and the remainder, of which there is a model in the collection of the British Museum, weighs about 277 carats (Maskelyne). The largest diamond in Europe is set on one end of the Russian sceptre; it has a yellow colour, and weighs 194¼ carats. The yellow Tuscan diamond of the Emperor of Austria weighs 139½ carats. The Koh-i-noor, one of the British crown diamonds, originally came from India, and when brought to this country in its rough state, weighed 186 carats. Owing to the imperfect character of its original cutting it had to be recut, and was thus reduced to 106 carats. The largest diamond ever found in the Brazils, termed the Star of the South, originally weighed 254½ carats, but was reduced by cutting to 127 carats. A Cape diamond of 971 carats in the rough condition has been found, and quite recently (1905) announcement has been made of the discovery of one of the unprecedented weight of 3,032 carats at the Premier Mine, Johannesburg. The diamonds in the possession of the Shah of Persia were undoubtedly derived from the plunder of Delhi by Nadir Shah. Their weight is unknown. According to Tavernier, the Great Mogul possessed a diamond which before cutting weighed 900 carats, but afterwards only weighed 279·6 carats.

Rough or small diamonds, which cannot be used as brilliants, are termed "Boart" and are employed for a number of other purposes. Their powder is largely used for the purpose of cutting diamonds and other precious stones, whilst the splinters are used for the purpose of writing upon glass, although they will not cut that substance. For the latter purpose a naturally-curved edge of the crystal is needed; the curved edge producing a deep slit determining the fracture of the glass with certainty, whilst the straight edges merely scratch the surface. Diamonds are also largely used in the construction of rock-boring tools.

435 *Graphite* was also known to the ancients, but up to the time of Scheele no distinction was made between it and the closely similar substance, sulphide of molybdenum, MoS_2, and, at that period, both these metal-like minerals which leave a mark on paper were termed indiscriminately *plumbago* or *molybdæna*. Graphite appears to have been first distinguished by Conrad Gessner in his work *De rerum fossilium figuris*, in 1565. A picture of a black-lead pencil occurs there, and underneath is written "Stylus inferius depictus ad scribendum factus est, plumbi cujusdam (factitii puto, quod aliquos stimmi Anglicum

vocare audio) genere, in mucronem derasi in manubrium ligneum inserti."[1]

For many years graphite was supposed to contain lead, whence the name plumbago, or black-lead. The former name seems to be derived from the Italian *grafio piombino*, which also, like the other name, graphite, from *γράφω*, I write, indicates its use.

In the year 1779 Scheele showed that molybdenum-glance is a totally different body from graphite, and that this latter when treated with nitric acid is converted into carbonic acid, so that it must be looked upon as a kind of mineral carbon.

Graphite occurs in nature tolerably widely distributed. It is usually found in lumps or nodules in granite, gneiss, and other crystalline rocks. The best graphite for the purpose of making black-lead pencils was that formerly found exclusively at Borrowdale in Cumberland, in green slate. This source is, however, now almost exhausted, the mines not having been worked for the last forty years. In the sixteenth and seventeenth centuries they were so productive as to yield an annual revenue of £40,000, although they were only worked a few weeks in the year for fear of exhausting the mine. Graphite is also found at Passau in Germany, in Bohemia and in Styria. It likewise occurs in many places in the United States, the deposits at Stourbridge, Mass., Ticonderoga (Essex County), Raleigh (N. Carolina), and Cumberland Hill (Rhode Island) being large enough to yield a considerable supply. By far the largest mine in the United States is the "Eureka Black-Lead Mine" at Sonora in California. The graphite here forms a layer of some twenty to thirty feet in thickness, and is so pure that it may be obtained in large blocks. Large quantities of graphite are also found in Ceylon, which supplies most of the material employed in this country. In Southern Siberia, to the west of Irkutsk, this substance occurs in considerable quantities in the Batougal mountains, and is largely exported to Europe.

Graphite commonly occurs in compact foliated or granular masses, but occasionally in small six-sided tables, which according to Kenngott belong to the hexagonal, but according to Nordenskjöld to the monoclinic, system. It has a steel-grey colour, an unctuous touch, and it is so soft that it gives a black streak on paper. Its specific gravity varies from 2·015 to 2·583,

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[1] "The pencil represented below, is made, for writing, of a certain kind of lead (which I am told is an artificial substance termed by some English antimony) sharpened to a point and inserted in a wooden handle."

and this considerable variation is due to the fact that almost all natural graphite contains more or less impurity which, when the graphite is burnt, remains behind as ash and consists of alumina, silica, and ferric oxide, with small traces of lime and magnesia.[1] It usually contains 0·5 to 1·3 per cent. of hydrogen,[2] a fact which seems to point to its organic origin. Graphite is a good conductor of heat and electricity, whilst the diamond is a non-conductor. Graphite, artificially prepared by the action of silicon on fused iron rich in carbon, commences to form carbon dioxide in oxygen at 570°, the production being rapid at 600°, whilst at 690° inflammation occurs,[3] but the temperature of ignition varies for different specimens of natural graphite. The specific heat at ordinary temperatures is 0·202 (Regnault), whilst at 978° it is 0·467 (Weber).

The artificial production of graphite by melting cast iron containing a large proportion of carbon, and allowing it to cool slowly, was first observed by Scheele in 1778. Cast iron contains a certain amount of carbon combined with iron; in the molten condition, however, it can dissolve a much larger quantity of carbon, up to as much as 4 per cent. of its weight, and this excess crystallises out as graphite when the metal cools. The costly crystalline grey pig-iron owes its peculiar properties as well as its appearance to the presence of graphite, and when this form of iron is dissolved in acid, scales of graphite remain as an insoluble residue.

Graphite also occurs in many meteoric masses, as, for instance, in the meteorite which fell in 1861 at Cranbourne near Melbourne, and this meteoric graphite is, according to Berthelot, identical in properties with iron-graphite. We may thus conclude that the meteoric mass in which it has been found has been exposed to a very high temperature.

According to Wagner, the black deposit which is formed by the spontaneous decomposition of hydrocyanic acid, CNH, contains graphite, as may be seen by washing the deposit with strong nitric acid, when the insoluble scales of graphite are left behind.[4] Another remarkable mode of production of graphite, most likely from cyanogen compounds, was first observed by Pauli[5] in the manufacture of caustic soda from the

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[1] Mène, *Compt. Rend.* 1867, **64**, 1019, 1867.

[2] Regnault, *Ann. Chim. Phys.* 1841, [3], **1**, 202.

[3] Moissan, *Compt. Rend.* 1902, **135**, 921.

[4] *Wagner's Jahresb.* 1869, p. 230.

[5] *Phil. Mag.* 1861, [4], **21**, 541.

black-ash liquors. These liquors are evaporated to a certain degree of consistency, and Chili saltpetre is added to oxidise the sulphur and cyanogen compounds present. Torrents of ammonia are thus evolved, and a black scum of graphite is observed to rise to the surface.

When the vapour of chloride of carbon is led over melted cast iron, ferric chloride is evolved, and carbon dissolves in the iron until it becomes saturated, after which hexagonal plates of graphite separate out.[1]

The carbon which occurs in crystalline boron remains as amorphous carbon when the diamond boron is heated to redness. When it is heated to whiteness it takes the form of graphite. Both diamond and amorphous carbon are converted into graphite at the temperature of the electric arc, and when the arc is maintained between two poles of amorphous carbon the negative pole is found to be largely converted into graphite.

When moistened with strong nitric acid and then strongly heated, many specimens of graphite possess the remarkable property of swelling up and leaving a very voluminous residue of finely divided graphite, in the same manner as mercuric sulphocyanide (Pharaoh's serpents). This property, however, is not common to all specimens of graphite, and it has even been proposed to divide the known graphites into two classes, those which give this nitric acid reaction being recognised as graphite, whilst those which do not, such as the graphite of the electric arc and that obtained from cast iron, are distinguished as graphitite.[2]

The intumescent variety may be prepared by fusing platinum in a carbon crucible in an electric furnace. When the ingot is treated with aqua regia a residue of graphite of this kind is left. It is also found in the interior of an ingot of cast iron which has been cooled by water, whilst the external layers only contain the non-intumescing variety. When intumescence takes place oxides of nitrogen and a little carbon dioxide are given off and a residue of pure graphite left, which is scarcely altered by further treatment with nitric acid. The intumescence is, therefore, probably due to the sudden evolution of gas produced by the action of traces of nitric acid remaining in the graphite upon a little amorphous carbon entangled among the plates of graphite.[3]

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[1] H. Deville, *Ann. Chim. Phys.* 1857 [3], **49**, 72.

[2] Luzi, *Ber.* 1891, **24**, 4085; 1892, **25**, 216. 1378; 1893, **26**, 890. Moissan, *Compt. Rend.* 1893, **116**, 608.

When graphite is repeatedly treated with fuming nitric acid and potassium chlorate it is converted into insoluble substances which contain both hydrogen and oxygen, known as graphitic acid (p. 805), whereas under the same treatment diamond is unaltered and amorphous carbon yields substances known as *humic acids*, which are soluble in water. This reaction provides a means of distinguishing graphite from the other allotropic forms of carbon, and is the basis of Berthelot's method[1] for estimating the proportions of the three varieties in a mixture.

When the electric arc is maintained between carbon poles, it is observed that, however powerful the current, a maximum degree of brightness is attained. This seems to indicate that the carbon of the pole volatilises at the temperature corresponding to this brightness. By heating a portion of the pole to this maximum temperature and then shaking it off into a calorimeter it has been found that the temperature of volatilisation of carbon is about 3,600°, and this is, therefore, the maximum temperature which can be attained in an electric furnace in which carbon poles are employed.[2]

None of the varieties of carbon appear to be capable of fusion under the ordinary pressure, but when heated in an electrical furnace they volatilise without melting, the vapour condensing to graphite.[3]

436 As already mentioned, many specimens of graphite intumesce when moistened with nitric acid and strongly heated. It is also found that when finely-powdered graphite is heated with a mixture of one part of nitric and four parts of strong sulphuric acid, or when a mixture of fourteen parts of graphite and one part of potassium chlorate is warmed with twenty-eight parts of strong sulphuric acid, the graphite assumes a purple tint, but on subsequent washing returns to its original colour. It contains now oxygen, hydrogen, and sulphuric acid, and when it is heated to redness swells up with a copious evolution of gas, and then falls to an extremely finely-divided powder of pure graphite, which has a specific gravity of 2·25.[4] This process is employed for the purpose of purifying natural graphite. With this object it is first ground, and the powder well washed in long troughs in order to remove as much as possible

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[1] *Ann. Chim. Phys.* 1870 [4], **19**, 399.

[2] Violle, *Compt. Rend.* 1892, **115**, 1273; 1895, **120**, 868.

[3] Moissan, *Compt. Rend.* 1894, **119**, 776.

[4] Brodie, *Ann. Chim. Phys.* 1855 [3], **45**, 351.

of the earthy matrix with which it is mixed. The graphite thus obtained is pure enough for many uses; but if it is required in the pure state, the powder must be treated with potassium chlorate and sulphuric acid as above described. The fine powder is then thrown upon water, on the surface of which it swims, whilst the earthy matters sink to the bottom. The foliated graphite answers best for this purpose, powdered graphite being more difficult to purify. This variety may, however, also be rendered pure if a small quantity of sodium fluoride be added to the mixture as soon as the evolution of chlorine and its oxides has ceased, the object of this addition being to remove the silica as silicon tetrafluoride.

Graphite is employed for a great variety of purposes. The Cumberland black-lead pencils, the first of their kind, were originally manufactured by cutting slips of graphite out of the solid block. Experiments were afterwards made for the purpose of making use of the graphite powder, which was fused with sulphur or antimony. The pencils thus prepared were, however, hard and gritty. A remarkable improvement in the manufacture, used up to the present day, was introduced by Comte. The powdered graphite is mixed with carefully-washed clay, and the mixture placed in short iron cylinders having an opening at the bottom. The semi-solid mass is then pressed through the hole and assumes the form of a fine thread, which can be cut up into the required lengths and used for pencil-making.

Another important application of graphite is for the preparation of the black-lead crucibles largely used in metallurgical operations, especially in the manufacture of cast steel. The Patent Plumbago Crucible Company at Battersea employ Ceylon graphite for the manufacture of their crucibles, whilst the graphite employed by Krupp of Essen in the manufacture of the crucibles in which his celebrated cast steel is melted is obtained from Bohemia. The finely-ground graphite is well mixed with Stourbridge fire-clay and water, so as to obtain a homogeneous mass; the water is then pressed out and the mass formed into blocks, which have to lie for many weeks. The plasticity of the mass is thus much increased. The crucible is next moulded by hand on a potter's wheel, or sometimes formed in a mould; it is then slowly dried, and afterwards ignited in a pottery furnace, being placed in saggers in order to prevent the combustion of the graphite. These crucibles are good conductors of heat, they do not crack readily on change of temperature, and they likewise possess a clean surface, so that the metal can be poured out completely.

Finely-divided graphite purified according to Brodie's process has been largely used for polishing gunpowder, especially the large grain, blasting, and heavy ordnance powder. This coating of black lead gives a varnish to the corn and prevents it from absorbing moisture. The explosive force of the powder is, however, somewhat diminished by this coating of graphite, for Abel has shown that the explosive force of unpolished powder being 107·6, the same powder polished with common graphite has an explosive force of 89·9, and when varnished with Brodie's graphite of 99·7.

The particles of the finely-divided and purified graphite adhere together when they are brought into close contact, as by great pressure, and the mass thus obtained may be used for pencil-making and for other purposes. The pressed graphite is found to conduct electricity very much more readily than the ordinary graphite, and better than gas-carbon. Thus, according to Matthiesen, its conducting power is eighteen times greater than that of natural graphite and twenty-nine times as great as that of the dense carbon used for the Bunsen's batteries. From this property, graphite powder is used largely in electrotyping, the moulds upon which it is desired to deposit the metal being covered with a fine coating of powdered graphite. This acts as a conductor of electricity, and a uniform coating of the metal is deposited upon it. Graphite is used not only for the purpose of preventing the rusting of iron objects but in some cases also instead of, or together with, oil for lessening the friction in running machinery.

437 *Amorphous Carbon.*—In early ages the attention of chemists was attracted to charcoal from the fact that it is a body which cannot be acted upon by any solvent. The supporters of the phlogistic theory made this substance a special study, because they believed that it contained more phlogiston than any other known body. This modification of carbon is produced when substances which contain that element are strongly heated in the absence of air. The amorphous carbon thus obtained has received various names which indicate its origin or mode of production, but the different varieties are identical in chemical properties. The chief forms which are thus distinguished are (1) lamp-black, (2) gas-carbon, (3) charcoal, (4) animal charcoal, and (5) coke. The last three of these usually

contain mineral matter which was originally present in the wood, bone, or coal from which they are derived. The substances known by these names also generally contain small amounts of both hydrogen and oxygen.

(1) *Lamp-black.* The luminosity of flame is probably due to the presence in it of intensely heated particles of carbon, which are deposited as soot on any cold surface held in the flame. When the burning substance is rich in carbon, the flame smokes even without its being cooled, and it does so the more strongly the smaller the supply of air. This fact is made use of for the purpose of preparing finely-divided amorphous carbon or lamp-black.

In the manufacture of lamp-black, tar, resin, turpentine, or petroleum is burnt in a supply of air insufficient to burn it completely, the smoky products of this imperfect combustion being allowed to pass into large chambers hung with coarse cloths, on which the lamp-black is deposited. The finest kind of lamp-black is obtained by suspending metallic plates over oil-lamps, or revolving over them metallic cylinders, on which the soot is deposited. It is purified by heating it in closed vessels, and is used for preparing Indian ink and in calico-printing for producing grey shades; while common lamp-black is employed as a black paint and for manufacturing printer's ink. Soot or lamp-black is, however, not pure carbon but contains about 80 per cent. of that element along with oily and fatty matters and a small amount of mineral matter, for it always contains appreciable quantities of hydrocarbons arising from the incomplete combustion of the tar. In order to remove these impurities it is not sufficient to ignite the lamp-black strongly. It must be heated to redness in a current of chlorine for a considerable length of time, the hydrogen then combining with the chlorine and the carbon remaining unacted upon.

(2) *Gas Carbon,* which, next to lamp-black, is the purest form of amorphous carbon, is formed in the preparation of coal-gas, and probably owes its origin to the decomposition, by the intensely heated walls of the retort, of the gaseous compounds of hydrogen and carbon which are evolved. It is found as a deposit in the upper portion of the retort in the form of an iron-grey mass, which is often so hard that it strikes fire like a flint. The portions of this carbon deposited on the sides of the retort contain no hydrogen, and have a specific gravity of 2·356,

whereas those lying further from the surface of the retort contain some hydrogen. Gas carbon is also obtained by passing olefiant gas, C_2H_4 (which is one of the chief constituents of coal-gas), through a red-hot porcelain tube. This form of carbon conducts heat and electricity well, and is used for the preparation of the carbon cylinders or plates employed in Bunsen's battery, and the carbon poles for the electric light.

(3) *Charcoal.*—This substance is obtained in the pure state by heating pure white sugar in a platinum basin. The carbon thus obtained is purified by ignition in a current of pure dry chlorine for 7 hours, well washed with hot distilled water, dried, and finally heated in a current of dry hydrogen till no more hydrogen chloride is evolved.[1] It is tasteless and possesses no smell. It is a good conductor of electricity and has a specific gravity of 1·57. Like the other modifications of carbon it is infusible and is insoluble in every solvent. Pure sugar-charcoal is used as a reducing agent, especially in the preparation of volatile metallic chlorides, and it is peculiarly valuable inasmuch as its freedom from silica prevents the formation of volatile tetrachloride of silicon.

Amorphous carbon is converted by many oxidising agents into complex soluble compounds, termed *humic acids*, which on further oxidation yield, among other products, oxalic acid, HO·CO·CO·OH, and mellitic acid, $C_6(COOH)_6$. (Vol. III. Part v. p. 374.) Both of these acids are formed by the action of alkaline potassium permanganate solution on amorphous carbon,[2] whilst mellitic acid is also formed by the oxidation of wood charcoal with concentrated sulphuric acid,[3] carbon dioxide, and sulphur dioxide being evolved at the same time (p. 391), and when a current of electricity is passed through a solution of caustic potash between carbon poles.[4] The aluminium salt of mellitic acid, known as honey-stone, occurs in seams of brown coal and is possibly formed by oxidation from that material.

The specific heat of amorphous carbon (wood charcoal) is 0·241.

On the large scale, wood charcoal is prepared in the same way from wood as is coke from coal. Charcoal-burning is a

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[1] Bone and Jerdan, *Journ. Chem. Soc.* 1897, 45.

[2] Schulze, *Ber.* 1871, **4**, 802, 806.

[3] Verneuil, *Compt. Rend.* 1894, **118**, 195.

[4] Bartoli and Papasogli, *Gazzetta*, 1883, **13**, 37.

very old process, and the simple methods which were originally adopted are carried on up to the present day. The method consists in allowing heaps of wood covered with earth or sods to burn slowly with an insufficient supply of air. It is usual to build up large conical heaps with billets of wood placed vertically and covered over with turf or moistened soil, apertures being left at the bottom for the ingress of air, and a space in the middle serving as a flue to carry off the gases (Fig. 176). The pile is lighted at the bottom and the combustion proceeds gradually to the top. Much care is needed in regulating the supply of air and the consequent rate of the combustion. One hundred parts of wood thus treated yield, on an average, sixty-one to sixty-five parts by measure, or twenty-five parts by weight, of charcoal. In Austria and Sweden charcoal is made from long

Fig. 176.

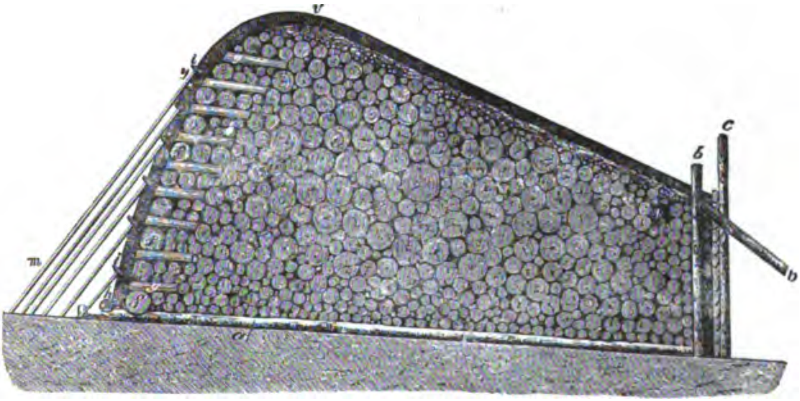

Fig. 177.

logs of fir-wood, which are placed horizontally in a rectangular pile (Fig. 177).

In countries like our own where wood is scarce, charcoal is obtained from small wood or sawdust by a more modern process. It consists in the carbonisation of the wood in cast-iron retorts, and in this process not only is charcoal obtained, but the volatile products, especially wood spirit, and pyroligneous acid, as well as tar, are collected.

Good charcoal possesses a pure black colour and a bright glittering fracture. When struck with a hard object it emits a sonorous tone and it burns without smoke or flame. The specific gravity of wood charcoal, when the pores are filled with air, varies between 0·106 (ash charcoal) and 0·203 (birch charcoal). Such charcoal will swim on water, but it sinks when the pores which were filled with air become filled with liquid, as the actual specific gravity of the solid itself is greater than water, varying according to the method of preparation but being always less than 2.

The properties and chemical composition of charcoal vary much according to the temperature to which the wood is heated. According to Percy,[1] wood becomes perceptibly brown at 220°, whilst at 280° it becomes after a time a deep brown-black, and at 310° it is resolved into an easily pulverisable black mass. Charcoal made at 300° is brown, soft, and friable, taking fire easily when heated to 380°; whilst that prepared at a high temperature is a hard, brittle substance, which does not take fire till it is heated to about 700°. The proportion of carbon contained in charcoal prepared at different temperatures varies considerably. That prepared at the lowest point contains much more of the volatile constituents of the original wood than the charcoal made at a red heat, though, as a matter of course, the yield of charcoal is greater at the low temperature. According to Violette[2] 100 parts of buckthorn-wood yield the following amounts of charcoal:—

At	250°	50	parts of	charcoal	containing	65	per cent.	carbon.
„	300°	33	„	„	„	73	„	„
„	400°	20	„	„	„	80	„	„
„	1500°	15	„	„	„	96	„	„

Thus charcoal, like lamp-black, as ordinarily prepared, never

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[1] *Metallurgy: Fuel*, p. 107.

[2] *Ann. Chim. Phys.* 1851, [3], **32**, 305.

entirely consists of pure carbon (Davy). The following table gives the composition of charcoal obtained at different temperatures.

	270°	350°	432°	1023°	1100°	1250°	1300°	1500°	Over 1500°
Carbon . . .	70·45	76·64	81·64	81·97	83·29	88·14	90·81	94·57	96·51
Hydrogen .	4·64	4·14	1·96	2·30	1·70	1·41	1·58	0·74	0 62
Oxygen with some nitrogen . . .	24·06	18·61	15·24	14·13	13·79	9·25	6·46	3·03	0·93
Ash	0·85	0·61	1·16	1·60	1·22	1·20	1·15	1·66	1·94
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100 00	100·00

The following results were obtained by Faisst.[1]

	Beech charcoal.	Hard charcoal, made in iron cylinders.	Light charcoal, from wood-gas-works.
Carbon	85·89	85·18	87·43
Hydrogen	2·41	2·88	2·26
Oxygen and nitrogen .	1·45	3·44	0·54
Ash	3·02	2·46	1·56
Water	7·23	6·04	8·21
	100·00	100·00	100·00

(4) *Animal Charcoal*, which is obtained by the carbonisation of animal materials, differs from that prepared from vegetable sources, inasmuch as it contains considerable quantities of nitrogen. *Bone-black* is obtained by charring bones in iron cylinders or retorts, and is formed as a by-product in the manufacture of animal, or Dippel's oil (*Oleum animale Dippelii*). Dry bones contain about 70 per cent. of inorganic material, consisting chiefly of calcium phosphate. This inorganic matter remains behind with the charcoal when the bones are charred, and thus the charcoal is deposited in an extremely finely-divided condition. It is probably for this reason that bone-black possesses a greater absorptive and decolorising power than wood charcoal. The presence of the calcium phosphate, however, prevents the application of this decolorising power of the charcoal to cases of acid liquids which dissolve the phosphate. In such cases it is necessary to make use of *blood charcoal*. This is obtained by evaporating four parts of fresh blood with one part of potassium carbonate, and heating the residue in a cylinder. The charred

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[1] Wagner, *Jahresb.* 1855, p. 457.

residue is then boiled out with water and hydrochloric acid, and again heated to redness in a closed vessel. The addition of potash serves the purpose of making the charcoal as porous as possible.

The following is an analysis of a good sample of dried animal charcoal.[1]

Carbon	10·51
Calcium and magnesium phosphates, calcium fluoride, &c.	80·21
Calcium carbonate	8·30
Other mineral matter	0·98
	100·00

438 Charcoal rapidly absorbs gases and vapours (Saussure), and possesses the remarkable property of precipitating certain substances from solution, and absorbing them in its pores (Lowitz, 1790), animal charcoal possessing this absorptive power in a much higher degree than common charcoal. The absorption seems to be almost entirely of a physical nature; thus, if a solution of iodine in iodide of potassium be shaken up with finely-divided charcoal, the iodine is completely withdrawn from solution, and in the same way certain metallic salts, especially basic salts, are decomposed when their solutions are filtered through charcoal. This power of withdrawing bodies from solution is exerted most effectually upon colouring matters and astringent principles. Thus, if a quantity of red wine (claret or port), or a solution of indigo in sulphuric acid, be shaken up and gently warmed with a quantity of freshly-ignited bone charcoal and the mixture filtered, the liquid which comes through is colourless. In the same way, if alcohol containing fusel oil be shaken up with animal charcoal, the characteristic smell of the fusel oil disappears. Wood charcoal is largely used for the latter purpose, whereas animal charcoal is employed for decolorising the juice of raw sugar. Animal charcoal is employed in a similar way in the purification of many organic compounds, although it not unfrequently happens that the compounds themselves are attracted by the porous charcoal. Occasionally this property is made use of for the separation of compounds which thus adhere to the charcoal, as, for instance, the alkaloids, from other bodies, these compounds being afterwards dissolved from the charcoal by

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[1] Thorpe's *Dictionary of Applied Chemistry*, vol. i. 171.

the addition of hot alcohol. Like many other porous substances both of these forms of charcoal possess the property of largely absorbing gaseous bodies. This power depends upon the fact that all gases condense in greater or less degree on to the surface of solid bodies with which they come in contact, and as charcoal is very porous, or possesses a very large surface to a given mass, its absorbent power is proportionately great. Charcoal, when exposed to the air, condenses large quantities of the latter upon its surface. This may be easily shown by attaching a piece of metal to it and sinking the mass in a cylinder filled with water. If the cylinder be now placed under the receiver of an air-pump and the air exhausted, a rapid stream of bubbles will be seen to rise in brisk effervescence from the charcoal. The remarkable absorptive power of charcoal for certain gases is also well illustrated by inserting a stick of recently calcined charcoal into a tube filled over mercury with dry ammonia gas. The gas is so quickly absorbed by the charcoal that the tube soon becomes filled with mercury. Another mode of showing a similar absorption of sulphuretted hydrogen gas is to plunge a small crucible filled with freshly-ignited and nearly cold powdered charcoal into a jar of sulphuretted hydrogen. This gas is then absorbed by the charcoal in such quantity that if it be removed when saturated and plunged into a jar of oxygen the charcoal will burst into vivid combustion, owing to combination occurring between the absorbed sulphuretted hydrogen and oxygen gases.

The absorptive power of wood charcoal for gases was first investigated by Saussure. In his experiments he made use of beech-wood charcoal which had been recently heated to redness and then cooled under mercury in order to remove the air from its pores. The following numbers were obtained by him :—

1 *volume of charcoal absorbs at* 12° *and under* 724 *mm. the following* (Saussure):

	Vols.		Vols.
Ammonia	90	Ethylene	35
Hydrochloric acid . . .	85	Carbon monoxide . .	9·42
Sulphur dioxide . . .	65	Oxygen	9·25
Sulphuretted hydrogen.	55	Nitrogen	6·50
Nitrous oxide	40	Hydrogen	1·25
Carbon dioxide	35		

Hunter,[1] who also made experiments on the same subject, found that one volume of charcoal absorbed the following quantities of gas at the temperature 0° and under a pressure of 760 mm.

Absorption of Gases by Charcoal (Hunter).

	Vols.		Vols.
Ammonia	171·7	Phosphine	69·1
Cyanogen	107·5	Carbon dioxide	67·7
Nitrous oxide	86·3	Carbon monoxide	21·2
Methyl chloride	76·4	Oxygen	17·9
Methyl ether	76·2	Nitrogen	15·2
Ethylene	74·7	Hydrogen	4·4
Nitric oxide	70·5		

The differences observed between these two series of experiments with the same gases are to be explained by the fact that the charcoals employed were not of equal porosity. Both series, however, show that the more readily the gas is condensable the more it is absorbed by charcoal, which seems to show that the gases condensed by charcoal undergo at any rate a partial liquefaction. This view is rendered possible by the observation of Melsen,[2] that when dry hydrogen is brought into contact with charcoal saturated with chlorine a considerable quantity of hydrochloric acid is formed, even when the experiment is carried on in complete darkness; and that when charcoal saturated with chlorine is brought into a Faraday's tube and the other limb placed in a freezing mixture, liquid chlorine is obtained. In a similar way ammonia, cyanogen, sulphur dioxide, sulphuretted hydrogen, and hydrobromic acid have been liquefied. This property of charcoal has been utilised by Dewar for isolating the small quantities of hydrogen, helium, and neon in air, as at very low temperatures it absorbs nitrogen, argon, and oxygen very rapidly, but has a much less effect on the above gases, the percentage amount of which in the residual gas is thereby largely increased.

Wood charcoal, like bone charcoal, has the power of absorbing the unpleasant effluvia evolved in the processes of decay and putrefaction as well as the moisture from the air. Stenhouse,[3]

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[1] *Phil. Mag.* 1863, [4], **25**, 364; 1865, **29**, 116.

[2] *Compt. Rend.* 1893, **76**, 81, 92.

[3] "On Charcoal as a Disinfectant," *Proc. Roy. Inst.* **2**, 53; also *Pharm. Journ.* **16**, 363.

who has investigated this subject, has shown that charcoal not only absorbs these gases and effluvia, but has the power, especially in contact with air, of oxidising and destroying them, inasmuch as when absorbed by charcoal these substances are brought into such close contact with the atmospheric oxygen, which is also absorbed by the charcoal, that a rapid oxidation is set up, and the odoriferous products of decomposition are rapidly resolved into carbon dioxide and water, and other simple compounds. This property is retained by the charcoal for a long time, and when it has been lost it can be renewed by ignition. Hence the use of charcoal filters has been suggested for preventing the foul sewer gases from polluting the air of the streets and houses, and charcoal respirators and ventilators have been proposed by Stenhouse as protections against the ingress of deleterious gases into the lungs. For the same reason, trays filled with heated wood charcoal, placed in the wards of hospitals or other infected apartments, are sometimes used for absorbing noxious emanations. Charcoal filters are also largely employed for filtering water for drinking purposes, as in its passage through the charcoal the water is decidedly improved in quality, not only organic and soluble colouring matters being removed as well as all suspended matter but the water undergoing aeration. Such filters do not, however, necessarily free the water from bacterial life; but may, on the other hand, increase its amount unless the filter is frequently sterilised. (See *ante*, p. 323.)

(5) *Coke.*—This substance remains behind when bituminous coal is heated to redness in absence of air. Coke is obtained as a by-product in the manufacture of coal-gas, but it is also specially manufactured in coke ovens, and sometimes by burning coal in heaps and stopping the combustion at a certain stage by quenching with water. When prepared by heating in covered ovens or kilns, the coke is harder, more lustrous, and less combustible than that obtained by burning in heaps. It is termed hard-coke or engine-coke, and is largely used for iron smelting, whereas the other variety is termed soft-coke or blacksmith's coke, and is the more combustible. Coke takes fire at a much higher temperature than common coal, and, when burning, gives rise to a very high temperature, but without the production of smoke, as it consists almost entirely of carbon. Coke not only contains the inorganic material, or ash, present in the coal from which it is manufactured, but

in addition small quantities of hydrogen, oxygen, nitrogen, and sulphur.

The amount of coke produced in Great Britain annually is estimated at about 11,000,000 tons.

COAL.

439 When vegetable matter decays in absence of air and under water, or in the earth, it undergoes a change similar to that which occurs when it is heated. Water, carbon dioxide, and methane, or marsh gas, are given off, and the residual material becomes richer in carbon. The fact of the occurrence of methane and carbon dioxide as products of decomposition is rendered evident by their presence in a highly compressed condition in the coal measures at the present day, from which the former is evolved as fire-damp in enormous quantities which often produce fatal accidents. It is in this way that the coals of various kinds, lignites, and peats have been formed. Their composition compared with that of cellulose is shown in the following table, the amount of mineral matter which is left behind as ash on combustion having been subtracted:—

——	Carbon.	Hydrogen.	Oxygen and Nitrogen.
Cellulose	50·00	6·00	44·00
Irish peat	60·02	5·88	34·10
Lignite from Cologne . .	66·96	5·25	27·76
Earthy coal from Dax . .	74·20	5·89	19·90
Cannel coal from Wigan .	85·81	5·85	8·34
Newcastle Hartley	88·42	5·61	5·97
Welsh anthracite	94·05	3·38	2·57

The above table shows that coal is a less pure form of carbon than wood charcoal. It consists of the more or less altered remains of a vegetable world which once flourished at various points on the earth's surface. The plants of the coal formation consist of Calamites, the representatives of the living Equisetums, of Lepidodendra, and Sigillariæ, which were the principal forest-trees, and which, though of gigantic dimensions, were true cryptogams, represented by the living Lycopods and Selaginellæ, and an important group of Conifers and Cycads, as yet not well understood, and chiefly known through their seeds, which are numerous and varied. Besides the remains of these arborescent types, bituminous coal contains spores and spore-cases of lycopods, and these often form the greater part of the coal. Ferns also formed an abundant undergrowth, many of these also having been representatives of the living tree-ferns.

In the passage into coal the original woody fibre and the resinous matter of the spores have not only undergone a loss of hydrogen and oxygen but they have at the same time become bituminised, so that for the most part all vegetable structure has disappeared and the coal possesses a fatty lustre and coarse slaty fracture, although many kinds of coal show distinct indications of a vegetable origin when examined in thin sections.

There are many different kinds of coal containing more or less of the hydrogen, oxygen, and nitrogen of the original vegetable growths. Cannel coal and boghead coal contain the most hydrogen, and anthracite contains the least, whilst the various kinds of bituminous coals lie between these extremes.

Anthracite Coal of all coals contains the largest percentage of carbon, and has therefore undergone the most complete change from woody fibre. It is found in the oldest deposits of the carboniferous series, especially in South Wales, Pennsylvania, and Rhode Island, and in smaller quantities in France, Saxony, and Southern Russia. It has a conchoidal fracture, possesses a bright lustre, often sub-metallic, an iron-black colour, and is frequently iridescent. It burns with a smokeless flame. In the coal-fields anthracite gradually passes into bituminous coal, becoming less hard and containing more volatile matter. Its specific gravity varies from 1·26 to 1·8.

The *Bituminous Coals* consist of a large number of varieties differing considerably from one another in their chemical composition, as also in their products of decomposition by heat. They have the common property of burning with a smoky flame when placed in the fire and yielding on distillation volatile hydrocarbons, tar, or bitumen, whence their name is derived.

The most important kinds of bituminous coals are (1) *caking coal*, which softens and becomes pasty or semi-solid in the fire, and yields, when completely decomposed, a greyish-black cellular mass of coke; (2) *non-caking coal*, agreeing with the last-named variety in all its external characters and even in its chemical composition, but burning freely without softening, and without any appearance of incipient fusion; the residue which it yields is not a proper coke, being either in powder or in the form of the original coal.

Cannel Coal, sometimes called parrot coal. This is a variety of coal differing from the preceding in texture and yielding usually more volatile matters and gas of a high illuminating power, and was therefore formerly largely employed in gas-making. At present, however, owing to the scarcity and consequently increased price of cannel coal its use for this purpose has been largely given up. Cannel coal is more compact than bituminous, possesses little or no lustre, does not show any banded structure, breaks with a conchoidal fracture and smooth surface; and has a dull black or greyish-black colour. Its name is derived from the fact that small fragments when lighted will burn with flame, and hence it was termed candle- or cannel-coal.

The tables on pages 749 to 751 give examples of the composition of the different forms of coal.

Connected with the true coals is a peculiar form, termed *Boghead Coal* or Torbane Hill mineral, which was first found near Bathgate in Linlithgowshire, and has since been observed in other places, especially in New South Wales. This deposit occurs in the carboniferous formation, but it is not properly speaking a coal, but belongs to the class of bituminous shales. Its specific gravity is lower than that of true coal, and it possesses a brown instead of a black colour. When completely burnt it leaves a residue of about 20 per cent. of ash, and when moderately heated in a retort, about 70 per cent. volatilises partly as gas, partly as more or less liquid or solid hydrocarbons. These are known under the name of *paraffin oils*, and are largely used for illuminating as well as for lubricating purposes, and for the preparation of solid paraffin.

Brown Coal or *Lignite* belongs to a different and more recent geological period than coal proper, being found in the tertiary formation. It consists of the remains of trees and shrubs, as ash, poplar, and others, which now exist on the surface of the earth. It possesses a brown colour and often exhibits a characteristic woody structure. Its specific gravity varies from 1·15 to 1·30.

NON-CAKING BITUMINOUS COALS.

Locality.	Sp. Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Water.	Coke.
South Staffordshire .	1·278	78·57	5·29	12·88	1·84	0·39	1·03	11·29	57·21
" " .	—	70·41	4·69	12·47	—	0·71	2·20	9·52	—
" " .	—	71·13	5·01	9·67	1·58	0·81	1·35	10·45	—
St. Helens, Lancashire	1·279	75·81	5·22	11·14	1·93	0·90	5·00	3·23	65·50
Scotland	—	76·08	5·31	13·33	2·09	1·23	1·96	—	—
"	—	80·63	5·16	10·61	1·33	0·84	1·43	—	—
"	—	80·93	5·21	10·91	1·57	0·63	0·75	—	—
Dowlais, S. Wales . .	—	89·33	4·43	3·25	1·24	0·55	1·20	0·79	—
" " . .	—	87·62	4·34	2·52	1·13	1·07	3·32	0·68	—
" " . .	—	82·60	4·28	3·44	1·28	1·22	7·18	0·78	—
Blanzy, France . . .	1·362	76·48	5·23	16·01	—	—	2·28	—	57·00
Pas de Calais	—	82·68	4·18	4·54	—	—	8·60	—	87·62
Hungary	1·423	73·38	3·86	11·65	—	0·58	10·53	3·06	76·33
Aix-la-Chapelle . . .	1·343	91·45	4·18	2·12	—	—	2·25	—	89·40

CAKING BITUMINOUS COALS.

Locality.	Sp. Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Water.	Coke.
Northumberland . .	—	78·65	4·65	13·66	—	0·55	2·49	—	—
,, . .	—	82·42	4·82	11·11	—	0·86	0·79	—	—
,, . .	1·276	81·41	5·83	7·90	2·05	0·74	2·07	1·35	66·70
,, . .	1·259	78·69	6·00	10·07	2·37	1·51	1·36	—	—
Nottinghamshire . .	—	77·40	4·96	7·77	1·55	0·92	3·90	3·50	63·18
Blaina, S. Wales . .	—	82·56	5·36	8·22	1·65	0·75	1·46	—	—
,, ,, . .	—	83·44	5·71	5·93	1·66	0·81	2·45	—	—
,, ,, . .	—	83·00	6·18	4·58	1·49	0·75	4·00	—	—
Epinal	1·353	81·12	5·10	11·25	—	—	2·53	—	63·60
Charleroi	—	86·47	4·68	5·30	—	—	3·55	—	84·43
Pas de Calais	—	86·78	4·98	5·84	—	—	2·40	—	77·05
Hungary	1·295	86·93	4·35	6·47	—	0·86	0·89	1·20	78·85

CANNEL COALS.

Locality.	Sp. Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Water.	Coke.
Wigan	1·317	84·07	5·71	7·82	—	—	2·40	—	59·00
"	1·276	80·07	5·53	8·08	2·12	1·50	2·70	0·91	—
Ashton-under-Lyne .	—	83·25	5·75	5·06	—	0·86	3·48	1·60	63·25
Tyneside	1·319	78·06	5·80	3·12	1·85	2·22	8·94	—	—
Mold, Wales	—	79·87	5·78	8·09	—	0·57	2·85	2·84	56·60
" "	—	77·81	8·47	6·32	—	0·71	6·01	0·68	27·92
Scotland	—	66·44	7·54	10·84	1·36	0·84	12·98	—	—
"	—	63·10	8·91	7·25	—	0·96	19·78	—	30·23

ANTHRACITE COAL.

Locality.	Sp. Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Water.	Coke.
Swansea, S. Wales .	1·348	92·56	3·33	2·53	—	—	1·58	—	—
South Wales	1·392	90·39	3·28	2·98	0·83	0·91	1·61	2·00	—
" "	—	87·02	3·14	2·16	0·90	0·67	6·11	—	—
Pennsylvania	1·462	90·45	2·43	2·45	—	—	4·67	—	—
"	—	92·59	2·63	1·61	0·92	—	2·25	—	—
"	—	84·98	2·45	1·15	1·22	—	10·20	—	—

Jet is a black variety of brown coal, compact in texture, and taking a good polish. Hence it is largely used in jewellery.

Earthy Brown Coal is another brown friable material, sometimes forming layers in beds of lignite, but it is not a true coal, inasmuch as a considerable portion of it is soluble in ether and benzene, and often even in alcohol, whereas true coal is nearly, if not quite, insoluble in these liquids.

Turf or *Peat* is a material which is being constantly formed by the decomposition of marsh plants, chiefly mosses, &c. It always contains nitrogenous compounds, which are the cause of the peculiar smell which it gives off on heating, is very rich in ash, and after drying in the air it still contains 15—20 per cent. of water.[1]

The World's Production of Coal.—The following table, abstracted from the Board of Trade Returns, gives the production of coal in the chief countries of the world for the year 1902.

OUTPUT OF COAL FROM THE CHIEF COAL-PRODUCING COUNTRIES IN 1902.

British Possessions.

United Kingdom . .	227,095,000	tons of 2,240 lbs.
British India . . .	7,424,000	„ „
Dominion of Canada .	6,422,000	„ „
New South Wales . .	5,942,000	„ „
Victoria	225,000	„ „
Western Australia . .	141,000	„ „
Queensland	502,000	„ „
Tasmania	50,000	„ „
New Zealand	1,363,000	„ „
Cape Colony	166,000	„ „
Natal	593,000	„ „
Transvaal	1,420,000	„ „

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[1] For further information on the subject of coal, lying beyond the scope of this work, we refer our readers to the following standard works:—Percy's *Metallurgy: Fuel* (London, 1875); Hull, *On the Coal Fields of Great Britain; Statistics of Coal*, by R. C. Taylor, 1855; Ronalds and Richardson's *Chemical Technology*, vol. i.; Ronalds, *On Fuel and its Applications; Jevons, The Coal Question; Report of the Royal Commission on Coal;* Thorpe's *Dictionary of Applied Chemistry*. A second Royal Commission on Coal has just published its report (Feb., 1905).

Foreign Countries.

United States . . .	269,277,000	tons of 2,240 lbs.
German Empire . .	107,474,000	tons of 2,204 lbs.
France	29,365,000	„ „
Belgium	22,877,000	„ „
Russia	15,503,000	„ „
Sweden	305,000	„ „
Spain	2,723,000	„ „
Austria.	11,045,000	„ „
Hungary	1,163,000	„ „
Japan	9,702,000	tons of 2,240 lbs.

The total coal production of the world, exclusive of Brown Coal or Lignite, is now about 790 million tons, of 2240 lbs., per annum, of which the United Kingdom produces rather less, and the United States rather more, than one-third.

440 *Heat of Combustion of Carbon.*—The heat of combustion of the different allotropic modifications of carbon when burnt to carbon dioxide varies considerably. For two different varieties of diamond, Favre and Silbermann[1] found that the heat evolved by the combustion of 1 gram is 7770 cal. and 7888 cal. respectively. Natural graphite gave 7797 cal. and artificial graphite from cast-iron 7762 cal., whilst amorphous wood charcoal evolved 8080 cal. The heat of combustion of amorphous charcoal burning to carbon monoxide only, is 2417 cal. per gram.

441 *Atomic Weight of Carbon.*—The atomic weight of carbon was ascertained by Dumas and Stas[2] by weighing the amount of carbon dioxide formed from known weights of diamond and graphite, when burnt in oxygen, the apparatus employed by them being shown in Fig. 178. To ensure the complete absence of carbon dioxide from the oxygen used, the latter was collected and preserved in a large Woulffe's bottle (*a*) over aqueous caustic potash, the gas being driven out as required by means of a dilute caustic potash solution (*b*). The oxygen then passed through a long wide tube filled to the point (*c*) with pumice-stone moistened with strong caustic potash solution, whilst at (*d*) it came in contact with pieces of dry solid caustic potash, and at (*e*) with glass moistened with boiled sulphuric acid, passing finally through a U tube, marked (*f*),

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[1] *Ann. Chim. Phys.* 1852, [3], **34**, 414.

[2] *Ibid.* 1841, [3], **1**, 1.

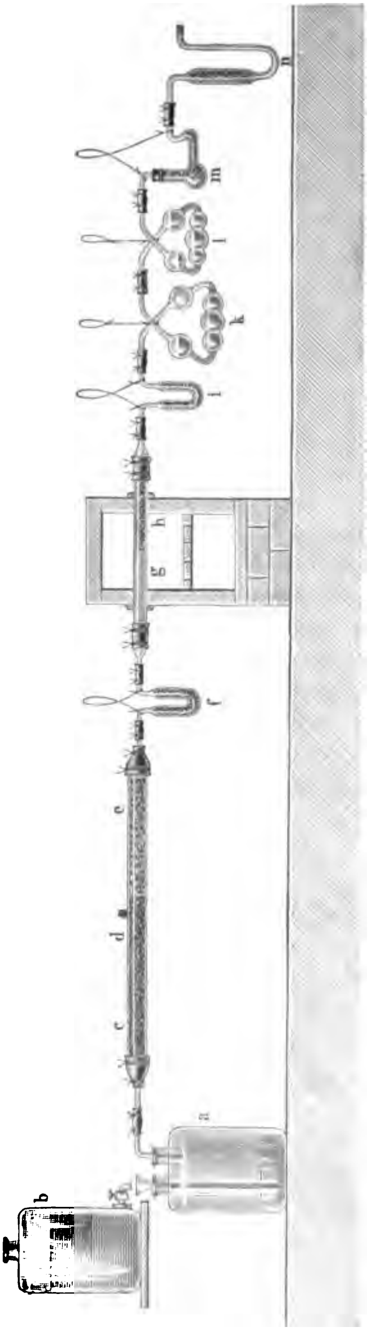

Fig. 178.

filled with pumice-stone moistened with sulphuric acid. This tube was weighed before and after the experiment. The pure dry oxygen then passed into a porcelain tube, which was heated to redness in a tube-furnace, the diamond or graphite undergoing combustion being placed at (*g*) in a platinum boat. The boat containing the substance was accurately weighed both before and after the experiment, inasmuch as even the purest diamond and graphite always leave on combustion traces of inorganic ash, and this must, of course, be subtracted from the total amount of substance taken. The other end of the tube contained, at (*h*), a quantity of perfectly oxidised copper scales, CuO, which served for the purpose of oxidising to carbon dioxide any monoxide which might be formed. The carbon dioxide then passed through the tube (*i*) containing pumice-stone moistened with sulphuric acid, and then into two Liebig's potash-bulbs (*k* and *l*). In order to be certain that the whole of the carbon dioxide was absorbed, and that no moist air passed away from the potash-bulbs, the excess of oxygen was passed through two tubes (*m* and *n*), the first of which contained pumice-stone moistened with potash, and the other solid potash. In this way five combustions of natural graphite were made, four of artificial graphite, and five of diamond, all of which gave closely agreeing results. The average of these showed that 11·91 parts of carbon combine with 31·76 parts of oxygen to form 43·67 parts of carbon dioxide. It has been shown in other ways that the formula of carbon dioxide is CO_2 (p. 788), and therefore the atomic weight of carbon is 11·91 if $O = 15·88$, or 12·00 if $O = 16$.

Almost at the same time, closely agreeing results by the same method were obtained by Erdmann and Marchand,[1] and this has also been used with agreeing results by later investigators.[2] Stas further obtained almost the same number by ascertaining the weight of oxygen required to convert carbon monoxide into the dioxide.[3]

The number 11·91 ($O = 15·88$) is therefore taken as the atomic weight of carbon. Scott[4] has, however, pointed out that the above methods all contain sources of error for which no correction has been made, which tend to make the result a little too high.

CARBON AND HYDROGEN.

442 All the elements hitherto described combine with hydrogen, but each of these elements possesses the power of forming only a small number of hydrides. Carbon, on the other hand, is distinguished from the foregoing elements, as well as from all the others, by the fact that it is capable of forming an extremely large number of hydrogen compounds. These substances are called *hydrocarbons*, and most of them are volatile bodies.

This peculiarity of carbon depends upon the fact that one atom possesses the property of combining with another atom of carbon, one or more of its four combining units being thus

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[1] *J. pr. Chem.* 1841, **23**, 159.

[2] Roscoe, *Compt. Rend.* 1882, **94**, 1180; Friedel, *Bull. Soc. Chim.* 1884, [2], **41**, 100; van der Plaats, *Compt. Rend.* 1885, **100**, 52.

[3] *Bull. Acad. Bruxelles*, 1849, **16**, 1.

[4] *Journ. Chem. Soc.* 1897, 550.

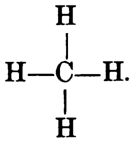
saturated, whilst the remaining combining units are capable of being saturated with hydrogen.

It has already been shown that other elements, such as oxygen and sulphur, possess the same property, though in a much smaller degree. Thus we know of no volatile compound which contains more than seven atoms of sulphur or of oxygen linked together in the same molecule. Disulphuryl chloride, $S_2O_5Cl_2$, is the compound which contains the largest number of atoms belonging to this group.

In the case of carbon such a limit has not, as yet, been found, derivatives containing as many as sixty carbon atoms directly united together having been already obtained. The number of hydrocarbons does not, however, depend merely upon the number of carbon atoms which can occur combined with one another, inasmuch as the atoms may saturate one another reciprocally by the union of one, two, or three of their own combining units. Notwithstanding this complexity of construction, the hydrocarbons may be classed in certain groups, each one of which can be represented by a general formula. Of these the three simplest are:—

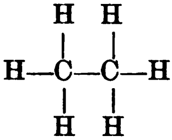
GROUP I. C_nH_{2n+2}.	GROUP II. C_nH_{2n}.	GROUP III. C_nH_{2n-2}.
Methane, CH_4.	—	—
Ethane, C_2H_6.	Ethylene, C_2H_4.	Ethine, C_2H_2.
Propane, C_3H_8.	Propylene, C_3H_6.	Propine, C_3H_4.
Butane, C_4H_{10}.	Butylene, C_4H_8.	Butine, C_4H_6.
Pentane, C_5H_{12}.	Pentylene, C_5H_{10}.	Pentine, C_5H_8.

The constitution of these compounds of carbon and hydrogen, or *hydrocarbons* as they are usually termed, is best understood by starting with the simplest, in which the four combining units of a single carbon atom are saturated by hydrogen. This is the well-known substance *methane* or *marsh gas*, and its constitution is represented by the graphic formula



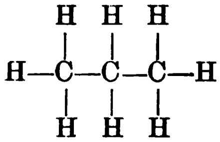
$$\begin{array}{c} H \\ | \\ H—C—H. \\ | \\ H \end{array}$$

If one atom of hydrogen in this compound be replaced by a carbon atom, and the remaining valencies of the latter saturated by hydrogen, we obtain a hydrocarbon having the composition C_2H_6, the constitution of which is as follows:—



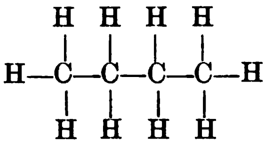
or $CH_3—CH_3$.

If, now, one of the hydrogen atoms in this hydrocarbon be replaced by a third carbon atom, and its remaining combining units saturated with hydrogen, we obtain a new substance, C_3H_8, its constitution being



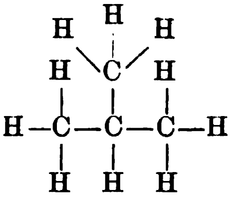
or $CH_3 . CH_2 . CH_3$.

The same process may again be carried out, but here it is not, as in the previous cases, immaterial which hydrogen atom is replaced by the added carbon atom, for these have not all an equal value. An examination of the graphic formula given above for C_3H_8 shows that two of the hydrogen atoms are combined with a carbon atom which is itself attached to two other carbon atoms, whilst the remaining six hydrogen atoms are combined with a carbon atom attached to only one other carbon atom. Hence according to the formula we can get the two following compounds of the composition C_4H_{10}:—

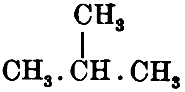


or

$CH_3 . CH_2 . CH_2 . CH_3$



or



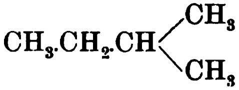
$$CH_3 . \overset{\overset{\textstyle CH_3}{|}}{C}H . CH_3$$

and in fact two and only two compounds of this composition have been experimentally obtained. Substances of this kind, which have the same percentage composition but different physical and chemical properties, are known as *isomerides.* Such cases are occasionally met with in the compounds of the other elements, as for example in the case of the potassium sodium sulphites (p. 397), but they are of far more frequent occurrence among the carbon compounds. Thus three different hydrocarbons having the formula C_5H_{12} are known, their formulæ being

(1)

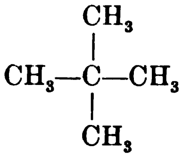
$$CH_3.CH_2.CH_2.CH_2.CH_3$$

(2)



$$CH_3.CH_2.CH\begin{cases}CH_3\\CH_3\end{cases}$$

(3)

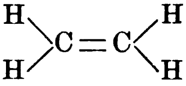


$$\begin{array}{c}CH_3\\|\\CH_3-C-CH_3\\|\\CH_3\end{array}$$

and the number of possible isomerides rapidly increases with the rise in the number of carbon atoms, no less than 799 different isomerides having the composition $C_{13}H_{26}$ being theoretically possible.

All the hydrocarbons derived in this manner from methane have the general formula C_nH_{2n+2}, and are usually termed the *paraffins.*

A different series of hydrocarbons, known as the *olefines,* and having the general formula C_nH_{2n}, contains two carbon atoms united together by two combining units, the simplest representative being ethylene, C_2H_4, the constitution of which is represented by the formula



$$\begin{array}{c}H\\H\end{array}>C=C<\begin{array}{c}H\\H\end{array} \quad \text{or} \quad CH_2=CH_2.$$

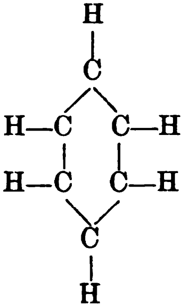
The hydrogen atoms of this hydrocarbon may be replaced by other carbon atoms in exactly the same manner as described under methane, giving rise to new hydrocarbons, of which the following may be taken as examples:—

Propylene.	α-Butylene.	β-Butylene.
$CH_3.CH=CH_2$	$CH_3.CH_2.CH=CH_2$	$CH_3.CH=CH.CH_3$

Another series, somewhat similar to the foregoing, having the general formula C_nH_{2n-2}, contains two carbon atoms united together by three combining units. The first member of this series, known as *acetylene*, has the constitution

$$CH \equiv CH.$$

In a fourth series of hydrocarbons the carbon atoms are united together in such a manner that they form a closed chain. The most important member, *benzene*, contains a closed chain of six carbon atoms, its constitution being represented as follows:—



It will be observed that in this formula only three valencies of each carbon atom are represented as saturated; the manner in which the remaining valencies are disposed is still a matter of discussion.

Almost all the other compounds of carbon may be regarded as derived from one or other of these numerous hydrocarbons; thus, for example, chloroform, $CHCl_3$, is methane in which three of the four hydrogen atoms have been replaced by chlorine, and alcohol, C_2H_6O, is ethane, C_2H_6, in which one atom of hydrogen has been replaced by the compound radical hydroxyl:—

$CH_3.CH_3$	$CH_3.CH_2.OH$
Ethane.	Alcohol.

Most of the substances occurring in the animal and vegetable kingdoms belong to the group of carbon compounds, and in addition to these an immense number of other derivatives containing this element have been prepared artificially, so that the total number of carbon compounds known is greater than that of all the other elements put together. For this reason they are separately treated of under the head of *Organic Chemistry*, which is now usually defined as the *Chemistry of the Hydrocarbons* *and their Derivatives.* In this volume only the simpler hydrocarbons, containing one or two atoms of carbon, will be considered.

METHANE, MARSH GAS, OR FIRE-DAMP, $CH_4 = 15{\cdot}91$.

443 This gas is found in the free state in nature, and its occurrence was observed in early times. Thus Pliny mentions the combustible gaseous emanations which occur in several districts, and Basil Valentine remarks upon the outbreaks of flame which occur in mines, and which are preceded by a suffocating damp (*Dampf*) or vapour. He does not consider that this vapour is combustible, but rather believes that the flame is emitted by the rocks for the purpose of destroying this poisonous vapour.

Methane, like some other combustible gases, was not distinguished from inflammable air, or hydrogen, until Volta, in the year 1776, showed that inflammable air, when burnt, required only one-fourth of the volume of oxygen which was needed for the complete combustion of methane, and that in this latter case alone was carbonic acid formed. In the year 1785, Berthollet proved that this gas contains both carbon and hydrogen, but it was at that time not distinguished from olefiant gas (or ethylene, C_2H_4). In 1805, William Henry clearly pointed out the difference between these two gases.

We have already seen that methane occurs free in nature. It is evolved, together with other hydrocarbons, in large quantities in petroleum springs. The holy fire at Baku on the Caspian Sea, which has been burning from the earliest historical times, is due to methane, mixed, according to Hess, with small quantities of nitrogen, carbon dioxide, and the vapours of petroleum. The gas which is evolved from the mud volcanoes of Bulganak in the Crimea has been shown by Bunsen[1] to consist of pure methane. The gases which escape in large quantities from the oil springs in Butler County, Pennsylvania, contain, according to Sadtler's analyses,[2] methane and its homologues, together with hydrogen. These gases are collected and carried by pipes to the rolling mills at Pittsburg, a distance of fifteen miles, where the gas is employed as a fuel. The natural gas obtained at

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[1] *Gasometry*, p. 147.

[2] *Amer. Philos. Soc.* 1876; see also Laurence Smith, *Ann. Chim. Phys.* 1876, [5], **8**, 566.

Heathfield, Sussex, contains 94·10 per cent. of methane and 2·97 per cent. of ethane.[1]

Enormous quantities of methane, or fire-damp, sometimes ignorantly termed "*sulphur*" by the miners, are evolved in coal-pits, due in all probability to a slow decomposition of the coal. Reservoirs of this gas in a highly compressed state are often met with pent up in the crevices and cavities of the coal measures. Some beds of coal are so saturated with gas that when they are cut it may be heard oozing from every pore of the rock, and the coal is called by the colliers *singing coal;* in other cases the gas escapes by what are termed *blowers,* and the mixture of gases frequently collects in the old workings or unventilated portions of the pit. Not unfrequently fire-damp bursts forth in large quantities from the seams of coal, or from the strata of clay which divide them. This is the frequent cause of the terrible accidents which sometimes, in spite of all care, will occur. The Lundhill colliery explosion, in 1857, was one of the most calamitous on record. The sudden escape of gas from a blower in a neighbouring colliery is thus described: "The fire-clay of the floor of the seam was seen to heave at different points along the face, and presently large fractures were made in it, through which gas was ejected with great violence, and with a sound very similar to the rushing of steam at a high pressure from a boiler. After the explosion at Lundhill, the pent-up gas still issued within the mine under such pressure as to support a column of water thirty feet high." The outburst of gas appears, sometimes at least, to be connected with a rapid fall in the barometer, the reduced atmospheric pressure enabling the gas to force its way out.[2] If he should escape from the effect of the explosion, the miner has still to fear its result, inasmuch as the gas in exploding renders ten times its own bulk of air unfit for respiration, and the *after-damp* or vitiated atmosphere produced by the explosion contains carbon dioxide in quantities sufficient to render it irrespirable. Hence the difficulty of descending into the pit after the explosion without proper precautions, or until a sufficient amount of ventilation has been re-established. The only satisfactory means of guarding against these sudden outbreaks in fiery pits is the establishment of a thorough and perfect system of ventilation, by means of which such an amount of

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[1] Dixon and Bone, *Proc. Chem. Soc.* 1903, 63.

[2] Scott and Galloway, *Proc. Roy. Soc.* 1872, **20**, 292.

air is brought into all parts of the workings as to render the formation of the inflammable mixture difficult or impossible, even when a sudden outbreak of gas occurs.

The escape of methane at the surface of the ground in the neighbourhood of the coal measures is frequently observed. This was first noticed by Thomson, at Bedley, near Glasgow, where a flame, once lighted, burnt for many weeks in succession. A similar case has been noticed by Pauli near St. Helens. The following analyses by Graham· show the composition of fire-damp :[1]—

	Sp. Gr.	Methane.	Nitrogen.	Oxygen.
Five-quarter seam, Gateshead colliery	0·5802	94·2	4·5	1·3
Bensham seam, Hebburn colliery	0·6327	—	—	0·6
Killingworth colliery	0·6306	82·5	16·5	1·0

Another instance of the formation of methane by the slow decomposition of vegetable matter, somewhat similar to that taking place in the coal seams, occurs in ponds or marshes, whence one of the names of the gas is derived. The gas-bubbles which rise when a stagnant pool containing decomposing leaves and vegetable matter is stirred, consist essentially of methane, which is mixed with carbon dioxide and nitrogen. The gas collected by Bunsen, in July, 1848, from a pond in the botanical gardens of Marburg, contained, after the absorption of carbon dioxide by caustic potash, the following:—

Methane	48·5
Nitrogen	51·5

The methane is probably formed by the bacterial fermentation of the cellulose of the plant debris. Methane also invariably occurs amongst the products of the dry distillation of organic bodies, and hence it is present in very considerable quantities in coal gas. Methane is produced in small quantity by the direct union of carbon and hydrogen at 1200°, and is the only hydrocarbon formed at this temperature; at higher temperatures ethane and acetylene are also formed.[2]

444 *Preparation.*—(1) In order to prepare methane an intimate mixture of one part of dried sodium acetate with four

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[1] *Phil. Mag.* 1864, [4], **28**, 437.

[2] Bone and Jerdan, *Journ. Chem. Soc.* 1897, 41; 1901, 1042.

parts of soda-lime (a mixture of caustic soda and lime) is heated. This is best accomplished in a tube of hard glass closed at one end and fitted with a delivery-tube at the other, or, in place of this, an iron tube or a copper flask may be employed. In order to obtain the gas as pure as possible, the mixture must only be heated to the point at which the gas begins to be evolved, but even with all care it is impossible to avoid the presence of some free hydrogen and some ethylene. This latter impurity may, however, be removed by passing the gas through a U-tube containing pumice-stone soaked in strong sulphuric acid. In a sample of the gas thus preparéd and purified, Kolbe[1] found 8 per cent. of hydrogen. The formation of methane from acetic acid is shown by the following equation:—

$$C_2H_3O_2Na + NaOH = Na_2CO_3 + CH_4.$$

(2) Chemically pure methane is obtained from zinc methyl, $Zn(CH_3)_2$, which is decomposed by water as follows:[2]—

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4.$$

(3) The pure gas is most readily obtained by the action of a zinc copper couple on a mixture of equal volumes of methyl iodide and alcohol, the reaction being assisted by gentle warming.[3]

(4) Methane can be obtained synthetically by passing a mixture of sulphuretted hydrogen and the vapour of carbon bisulphide over red-hot copper:[4]—

$$2SH_2 + CS_2 + 8Cu = CH_4 + 4Cu_2S.$$

(5) The same gas is likewise formed when a mixture of carbon monoxide and hydrogen is exposed to the action of the electric induction spark:[5]—

$$CO + 3H_2 = CH_4 + H_2O.$$

The same reaction takes place when the mixed gases are passed over reduced nickel, heated to 250°, the nickel finally remaining unchanged. A mixture of one volume of carbon dioxide and four volumes of hydrogen is also converted into

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[1] *Ausführl. Lehrb. Org. Chemie*, i. 275.

[2] Frankland, *Phil. Trans.* 1852, [2], 417.

[3] Gladstone and Tribe, *Journ. Chem. Soc.* 1884, 154.

[4] Berthelot, *Compt. Rend.* 1856, **43**, 454.

[5] Brodie, *Proc. Roy. Soc.* 1873, **21**, 245.

methane in contact with nickel, which in that case must be heated to about 350°.[1]

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

(6) Pure methane is formed by the action of water on aluminium carbide,[2] and it is also produced in the same manner mixed with other hydrocarbons from many other metallic carbides.

Properties.—Methane is a colourless, odourless gas, which has a specific gravity of 0·559; it is very sparingly soluble in water, its solubility from 6° to 20° being obtained from the equation:

$$c = 0{\cdot}05449 - 0{\cdot}0011807t + 0{\cdot}000010278t^2.$$

It dissolves more readily in alcohol, the solubility between 2° and 24° being found from the equation:

$$c = 0{\cdot}522586 - 0{\cdot}0028655t + 0{\cdot}0000142t^2.$$

The gas was first liquefied by Cailletet[3] in 1877; the liquid boils at −155° to −156° under the ordinary pressure, and at −73·5° under a pressure of 56·8 atmospheres,[4] and has at −164° a specific gravity of 0·415,[5] the critical temperature being −99·5°. It burns with a slightly luminous flame, the illuminating power, when tested under suitable conditions, being equivalent to five candles as compared with an illuminating power of 14—20 candles given by ordinary coal-gas.[6] When burnt in such a manner that the temperature of the flame is very high, as in a regenerative burner, the illuminating power is much greater. When mixed with twice its volume of oxygen it explodes in contact with a flame, the detonation being even more violent than in the case of a mixture of hydrogen and oxygen. Its heat of combustion per molecule in grams at 18° is 211,930 cal.

Methane is an extremely stable compound and when exposed to a temperature at which hard glass softens is only decomposed to a very slight extent. When the sparks from a strong induction coil are passed through the gas, or when it is

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[1] Sabatier and Senderens, *Compt. Rend.* 1902, **134**, 514.

[2] Moissan, *Compt. Rend.* 1894, **116**, 16.

[3] *Jahresb.* 1877, 221.

[4] Wroblewski, *Jahresb.* 1884, 197.

[5] Olszewski, *Jahresb.* 1887, 72.

[6] Wright, *Journ. Chem. Soc.* 1885, 200.

exposed to the action of the electric arc, it is partially dissociated into carbon and hydrogen, acetylene being also formed.

ETHANE, $C_2H_6 = 29{\cdot}82$.

445 This gas is invariably present in the gaseous discharge accompanying petroleum in the oil springs of Pennsylvania, and is dissolved in considerable quantities in the liquid hydrocarbons.[1]

Preparation.—(1) Ethane is readily obtained by treating ethyl iodide with zinc and water under pressure at a temperature of 150°;[2] thus:—

$$Zn + C_2H_5I + H_2O = ZnO + HI + C_2H_6.$$

The reaction is much more simply and readily carried out by the action of a zinc-copper couple on a mixture of ethyl iodide and alcohol.

(2) The same gas is produced when an electric current is passed through a concentrated solution of potassium acetate:[3]—

$$2C_2H_3O_2K + H_2O = C_2H_6 + K_2CO_3 + CO_2 + H_2.$$

Carbon dioxide and ethane are evolved at the negative pole, whilst hydrogen is set free at the positive pole.

It is also formed together with methane by passing a mixture of ethylene and hydrogen over reduced nickel heated to 325°.[4]

Properties.—Ethane is a colourless and odourless gas, slightly soluble in water, but more soluble in alcohol. According to Schickendantz, its coefficient of absorption in water is:

$$c = 0{\cdot}094556 - 0{\cdot}0035324t + 0{\cdot}00006278t^2.$$

It has a specific gravity of 1·036, and on cooling condenses to a liquid which boils at − 93° and freezes below − 123°. The critical temperature of the gas is 35° and the critical pressure 45·2 atm. It burns with a luminous flame, the illuminating power being about half that of ethylene burnt under similar conditions.[5] The heat of combustion (for 1 mol. in grams) is 370,440 cal.

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[1] Ronalds, *Journ. Chem. Soc.* 1851, 54.

[2] Frankland, *Journ. Chem. Soc.* 1850, 263.

[3] Kolbe, *Annalen*, 1849, **69**, 257.

[4] Sabatier and Senderens, *Compt. Rend.* 1897, **124**, 1358.

[5] Frankland, *Journ. Chem. Soc.* 1885, 237.

ETHYLENE, OR OLEFIANT GAS, C_2H_4.

446 This gas appears to have been discovered by Becher, who obtained it by heating alcohol with sulphuric acid. His observations were, however, considered to be erroneous up to the time of Priestley, who, in his *Experiments and Observations on Air*, mentions that Ingenhouss had seen such a gas prepared by a certain Enée in Amsterdam. The properties of olefiant gas were accurately studied in the year 1795 by Deimann, Paets van Troostwyk, Bondt, and Lauwerenburgh.[1] These Dutch chemists found that the gas obtained from alcohol and sulphuric acid was totally different from ordinary inflammable air, and that it contained both hydrogen and carbon. The difference between marsh gas and olefiant gas was first pointed out by William Henry in 1805,[2] and his view of the composition of the gas was borne out by the subsequent experiments of Dalton, Davy, and Berzelius. In those days, marsh gas and olefiant gas were the only hydrocarbons known, so that, their specific gravities being very different, they were termed the light- and the heavy-carburetted hydrogen respectively.

Preparation.—Ethylene is usually prepared by heating alcohol with strong sulphuric acid. Twenty-five grams of alcohol and 150 grams of sulphuric acid are brought into a flask of from two to three litres in capacity (see Fig. 179), and the mixture heated till the evolution of gas begins. By means of a funnel-tube, furnished with a stopcock, *b*, a mixture of equal volumes of alcohol and sulphuric acid is then allowed to drop into the flask.[3] The liquid froths up considerably, and care must be taken in heating to avoid its boiling over. To purify the gas thus obtained it must be first washed through concentrated sulphuric acid, and afterwards through caustic soda contained in the Woulffe's bottles, *c* and *d*, the alcohol vapour, carbon dioxide, and sulphur dioxide always present being thereby removed. It may then be collected over water and preserved in a gas-holder.

In place of sulphuric acid, tribasic phosphoric acid may also be employed with advantage, as the action takes place without undue frothing, and the gas evolved is free from carbon dioxide and sulphur dioxide: 50–60 c.c. of syrupy phosphoric acid are placed in a distilling flask, and the water boiled off until the

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[1] *Crell. Ann.* 1795.

[2] *Nicholson's Journal*, 1805.

[3] Erlenmeyer and Bunte, *Annalen*, 1873, **168**, 64.

temperature of the liquid is 200°, when alcohol is allowed to enter drop by drop through a tube dipping to the bottom of the flask. The gas is conducted through a small vessel cooled with ice which retains ether, alcohol, and traces of an oily liquid.[1]

Properties.—Ethylene is a colourless gas, possessing a peculiar ethereal smell; it is only slightly soluble in water, but is more so in alcohol; its solubility in water between 5° and 21° is expressed by the following equation (Pauli):—

$$c = 0{\cdot}25629 - 0{\cdot}00913631t + 0{\cdot}000188108t^2$$

Its specific gravity is 0·9784. It condenses to a colourless liquid which boils at −103·5°, and solidifies to a crystalline mass at −169°, the critical temperature being 9°, and the critical pressure 58 atmospheres. The liquid has a specific gravity of 0·335 at 8°.

FIG. 179.

Ethylene is readily inflammable, and burns with a brightly luminous flame, the illuminating power being about 70 candles[2] for the rate of 5 cub. feet per hour. The heat of combustion (for 1 mol. in grams at 18°) is 333,350 cal. When mixed with three times its volume of oxygen and ignited it explodes with extreme violence.

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[1] Newth, *Journ. Chem. Soc.* 1901, 915.

[2] Frankland, *Journ. Chem. Soc.* 1885, 237.

One very characteristic property of ethylene is its power of uniting with an equal volume of chlorine to form a heavy colourless liquid termed ethylene dichloride, $C_2H_4Cl_2$, or Dutch liquid, it having been first observed by the four Dutch chemists already named. From this property, indeed, the gas derives its name. It was originally termed *gaz huileux*, but this name was afterwards changed by Fourcroy to *gaz oléfiant*. When brought in contact with strongly ozonised oxygen, ethylene detonates very powerfully. In order safely to exhibit this property, a current of the gas is allowed to pass through a wide tube about 10 mm. in diameter, whilst ozonised oxygen is allowed to enter into this by means of a narrow tube, which is inserted into the wider tube to a distance of one centimetre. As soon as the ozonised oxygen comes in contact with the olefiant gas a detonation occurs, usually accompanied by the formation of white fumes.[1]

ACETYLENE, $C_2H_2 = 25{\cdot}82$.

447 This gas was discovered and its composition determined in 1836, by Edmund Davy,[2] who prepared it by treating with water the black mass obtained in the manufacture of potassium. The existence of this gas was afterwards observed by some other chemists, but it was not until the year 1859 that Berthelot[3] investigated it completely. Acetylene is produced mixed with other substances by the incomplete combustion of many volatile organic substances, especially of ethylene, coal-gas, and other hydrocarbons, as well as the vapours of alcohol, ether, &c., and also when such gases or vapours are passed through red-hot tubes.

Acetylene is also produced directly from its elements in an electric arc formed between carbon poles in an atmosphere of hydrogen. Smaller quantities of methane and ethane are simultaneously produced, the composition of the gas when equilibrium is attained being as follows:[4]—

Hydrogen	90—91	per cent.
Acetylene	7— 8	„
Methane	1·25	„
Ethane	0·75	„

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[1] Houzeau and Renard, *Compt. Rend.* 1873, **76**, 572.

[2] *Reports of British Association*, 1836, p. 62.

[3] *Ann. Chim. Phys.* 1859, [3], **57**, 82.

[4] Bone and Jerdan, *Journ. Chem. Soc.* 1901, 1062.

Acetylene may also be prepared by heating ethylene bromide with alcoholic potash, when the following reactions take place:

$$C_2H_4Br_2 + KOH = C_2H_3Br + KBr + H_2O.$$
$$C_2H_3Br + KOH = C_2H_2 + KBr + H_2O.$$

To remove any vapours of the volatile bromethylene, the gases evolved are passed through a second flask containing boiling alcoholic potash.

The method now employed for the preparation of acetylene consists in the action of water on calcium carbide, CaC_2, which is at present manufactured commercially for this purpose, acetylene being employed to a considerable extent as an illuminating gas. Its formation in this manner was first observed by Wöhler.[1]

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

The reaction takes place at the ordinary temperature, and the resulting gas is purified from volatile sulphur and phosphorus compounds, derived from impurities in the carbide, by passing it through solutions of chromic acid and bleaching powder. Many other metallic carbides also yield acetylene on treatment with water, either alone or mixed with other hydrocarbons. The manufacture of acetylene for illuminating purposes will be described in the chapter on the Gas Industry.

Properties.—Acetylene, when perfectly pure, has a pleasant, ethereal odour, but owing to the presence of certain impurities it usually has a very unpleasant smell, similar to that observed when a Bunsen burner "burns down," and this odour was formerly attributed to acetylene itself. It is poisonous, but in the pure state is less so than ordinary coal-gas. On cooling it condenses to a liquid which solidifies at −81°, whereas the vapour pressure does not fall to that of the atmosphere until −85° according to Villard,[2] or −83·8° according to Ladenburg and Krügel,[3] so that at atmospheric pressure the solid passes at once into the gaseous form. It burns in the air with an intensely luminous flame, giving, under suitable conditions, a light of 240 candles calculated to the rate of 5 cubic feet per hour. It is somewhat soluble in water, 1 vol. of the latter dissolving 1·1 vols. of

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[1] *Annalen*, 1862, **124**, 267.

[2] Villard, *Compt. Rend.* 1895, **120**, 1262.

[3] *Ber.* 1899, **32**, 1818.

acetylene at the ordinary temperature, but is almost insoluble in saturated salt solution. Alcohol dissolves six times its volume of the gas, and it is extremely soluble in acetone, especially under pressure. It combines with ice-cold water under pressure forming a crystalline hydrate, $C_2H_2,6H_2O$.[1]

Like ethylene it combines readily with the halogens, yielding with bromine the *dibromide*, $C_2H_2Br_2$, and the *tetrabromide*, $C_2H_2Br_4$. When mixed with excess of hydrogen and passed over platinum black at the ordinary temperature it is converted into ethane, whilst if the acetylene is in excess, ethylene is also formed. At 180° the reaction is much more complex, a mixture of liquid hydrocarbons being obtained in addition to the above gases, and a similar series of reactions takes place when the mixture is passed over iron, copper, nickel, or cobalt.[2]

The formation of acetylene from its elements takes place with absorption of heat,

$$\underset{\text{solid}}{2C} + \underset{\text{gas}}{2H} = \underset{\text{gas}}{C_2H_2} - 47{,}700 \text{ cal.}$$

Like many other endothermic compounds, when subjected to the shock given by an explosion of fulminate of mercury, the gas undergoes decomposition into its elements. At atmospheric pressure the decomposition is only partial and the explosion wave is not propagated through the whole of the gas, but at pressures exceeding two atmospheres the whole of the gas present is decomposed with a violent detonation.

Acetylene forms characteristic derivatives with certain metals. When the gas is passed over potassium, hydrogen is evolved, and potassium derivatives having the composition C_2HK and C_2K_2 are formed. These substances are black powders, which are decomposed by water with explosive violence, acetylene being reproduced.

The copper and silver derivatives of acetylene are readily obtained by passing the gas through an ammoniacal solution of silver nitrate or cuprous chloride. *Silver acetylide*, C_2Ag_2 or C_2Ag_2,H_2O, is thus obtained as a white precipitate, which is extremely explosive when dry; whilst *cuprous acetylide*, C_2Cu_2 or C_2Cu_2,H_2O, has a blood-red colour, and is likewise very

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[1] Villard, *Compt. Rend.* 1895, **120**, 1262.

[2] Sabatier and Senderens, *Compt. Rend.* 1899, **128**, 1173; 1900, **130**, 1559; 1900, **131**, 40.

explosive. Neither salt is attacked by water, but on addition of acids they at once evolve acetylene :

$$Cu_2C_2 + 2HCl = C_2H_2 + Cu_2Cl_2.$$

The preparation of these compounds may be carried out by means of the apparatus shown in Fig. 180, which likewise serves to prove the presence of acetylene in the products of the incomplete combustion of coal-gas. A bent funnel is placed over a Bunsen burner in which the flame is burning down, and the gases are aspirated through the cylinders *a* and *b*, which may be filled either with ammoniacal silver nitrate or ammoniacal cuprous chloride.

Fig. 180.

With solutions of silver salts alone, or with ammoniacal solution of the chloride, acetylene yields precipitates having the general formula C_2Ag_2,AgR, where R is a monovalent acid radical.[1]

CARBON AND THE HALOGENS.

448 Carbon combines directly with fluorine forming gaseous *carbon tetrafluoride*, CF_4, the reaction taking place spontaneously at the ordinary temperature with the less dense forms, whilst the more compact varieties must be heated to 50—100°. The

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[1] Berthelot and Delépine, *Compt. Rend.* 1899, **129**, 361.

remaining halogens do not combine directly with carbon, but a number of compounds of these elements with carbon can be obtained by indirect methods, as well as a much larger number of substances containing hydrogen in addition. These compounds are usually described under the head of Organic Chemistry, and only those containing one atom of carbon combined with four halogen atoms will be here considered.

Carbon tetrachloride, CCl_4, is the ultimate product of the action of chlorine on methane, the four atoms of hydrogen being successively replaced by chlorine with successive formation of the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. It is most readily prepared by passing dry chlorine through carbon bisulphide containing dissolved antimony trichloride, $SbCl_3$, the latter being converted into the pentachloride, which then acts on the carbon bisulphide as follows:[1]—

$$CS_2 + 2SbCl_5 = CCl_4 + 2SbCl_3 + 2S.$$

Carbon tetrachloride is a colourless, mobile liquid, which has a specific gravity of 1·6084 at 0°, boils at 76·74°, and has a smell similar to that of chloroform. It is not decomposed by water.

Carbon tetrabromide, CBr_4, is prepared by heating a mixture of 2 parts of carbon bisulphide, 14 parts of bromine, and 3 parts of iodine in a sealed tube for 48 hours at 250°, the cooled product being then distilled with addition of caustic soda.[2] It crystallises from alcohol in white glistening tablets, having an ethereal smell; it has a specific gravity of 3·42 at 14°, melts at 91°, and boils with partial decomposition at 189·5°.

Carbon tetriodide, CI_4, is obtained by dropping carbon tetrachloride diluted with carbon bisulphide on to aluminium iodide cooled to 0°, the chlorine of the tetrachloride being replaced by iodine.[3] It forms dark red regular octahedra, which decompose slowly in the air into carbon and iodine, the change taking place rapidly at 100°.

CARBON AND OXYGEN.

449 Carbon forms two oxides, both of which are gaseous :—

Carbon monoxide, CO.
Carbon dioxide, CO_2.

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[1] Hofmann, *Journ. Chem. Soc.* 1861, 62.

[2] Bolas and Groves, *Journ. Chem. Soc.* 1870, 154, 161; 1871, 773.

[3] Gustavson, *Compt. Rend.* 1874, **78**, 882.

CARBON MONOXIDE, OR CARBONIC OXIDE, $CO = 27{\cdot}79$.

This compound, which is commonly known as carbonic oxide, was first obtained by Lassone by heating zinc oxide with charcoal.[1] He found that a combustible gas was thus given off which burned with a blue flame, and when mixed with air did not explode, as was usually the case with inflammable air. Lavoisier (1777) obtained the same gas by heating alum and charcoal together, and found that on combustion it yielded carbonic acid. In spite of these observations, the gas was for a long time mistaken for hydrogen, and Priestley in 1796 showed that iron scale (oxide of iron), when heated with well-calcined charcoal, gives out an inflammable air, whereas according to Lavoisier's theory it ought only to give carbonic acid. This fact was, in Priestley's opinion, opposed to the antiphlogistic system, whilst it supported the view that the oxides contain water, and that inflammable air is phlogisticated water, and this was corroborated by the fact that when steam is led over red-hot charcoal it is phlogisticated to inflammable air. This conclusion was one which upholders of the Lavoisierian system found difficult to disprove, and they were driven to assume that hydrogen was still contained even in the most strongly heated charcoal; this fact, however, Priestley most satisfactorily proved to be incorrect in his last work, *The Doctrine of Phlogiston Established*, published in 1800.

In the same year Cruikshank was engaged with the examination of this same gas, which he obtained by heating carbon with different metallic oxides. From its comparatively high specific gravity he concluded that this gas was not a hydrocarbon, as others had assumed it to be. When burnt with oxygen it yielded no water, and nothing but an almost equal volume of carbon dioxide, whilst the oxygen which was needed for its combustion was less in volume than that contained in the carbonic acid gas formed. Hence he concluded that it must be an oxygen compound, and therefore gave to it the name of "gaseous oxyde of carbone." Clément and Désormes[2] soon after confirmed Cruikshank's results; they determined the composition of carbonic oxide more accurately than he had done, and found that it is likewise formed when carbon dioxide is led over red-hot charcoal.

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[1] *Mem. Paris. Acad.* 1776.

[2] *Ann. Chim.* 1802, **38**, 285.

450 *Preparation.*—Carbon monoxide can be prepared in various ways. (1) It is formed when zinc oxide, ferric oxide, manganese dioxide, and many other oxides are heated with charcoal; it is also formed when chalk (calcium carbonate), magnesite (magnesium carbonate), and other carbonates are heated with metallic zinc or iron filings; the decomposition which takes place in these cases is represented by the following equations:—

$$ZnO + C = Zn + CO.$$
$$CaCO_3 + Zn = CaO + ZnO + CO.$$

(2) Carbon monoxide is also formed when carbon is burnt in a limited quantity of oxygen, or by the action of carbon dioxide on heated charcoal.

$$CO_2 + C = 2CO.$$

The latter reaction does not take place below 600°, and then only in presence of moisture (p. 777). As the temperature is increased above 600°, moist carbon dioxide is partially converted into the monoxide, an equilibrium between the two gases being obtained at any particular temperature. The percentage of carbon monoxide in the mixed gas increases with the temperature, the following figures having been obtained by Boudouard at various temperatures:—

	Percentage Composition of Gas after attaining equilibrium.	
$t°$	CO_2.	CO.
650°	61	39
800°	7	93
925°	4	96

The same equilibrium is obtained at corresponding temperatures, when carbon monoxide is allowed to react with metallic oxides such as those of iron, nickel, and cobalt.[1]

(3) When oxalic acid or an oxalate is heated with concentrated sulphuric acid, a mixture of equal volumes of carbon monoxide and carbon dioxide is evolved, thus:—

$$C_2O_4H_2 = H_2O + CO + CO_2.$$

The carbon dioxide may readily be separated from the carbon monoxide either by passing the mixed gases through a solution of caustic soda or by collecting the mixture over water rendered alkaline by this substance.

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[1] *Compt. Rend.* 1899, **128**, 822, 824, 1522, 1524.

(4) Pure carbonic oxide is evolved when formic acid or a formate is heated with concentrated sulphuric acid:—

$$CH_2O_2 = CO + H_2O.$$

On the other hand, carbonic oxide can be converted into formic acid by heating it with caustic potash, potassium formate being produced (Berthelot):—

$$CO + \left.\begin{matrix}H\\K\end{matrix}\right\}O = \left.\begin{matrix}COH\\K\end{matrix}\right\}O.$$

(5) Carbon monoxide can be readily prepared in quantity by heating finely powdered potassium ferrocyanide with from 8 to 10 times its weight of strong sulphuric acid;[1] in this reaction, potassium sulphate, ammonium sulphate, and iron sulphate are formed, the following equation representing the decomposition:—

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4.$$

The water required for the reaction is contained in the ferrocyanide itself, which crystallises with three molecules of water, and also in the commercial acid, which invariably contains some. The mixture must be heated slowly, as otherwise the reaction, after once commencing, takes place with uncontrollable rapidity. According to Grimm and Ramdohr[2] it appears that sulphur dioxide and carbon dioxide are evolved in the beginning of the reaction, but afterwards pure carbon monoxide is given off. Commercial potassium cyanide may also be employed in place of the ferrocyanide.[3]

(6) Carbonic oxide may be readily prepared by passing carbon dioxide over zinc dust heated in a glass tube to rather less than a red heat, the resulting gas being washed through caustic soda.[4]

This reaction is sometimes made use of for the preparation of the gas on the large scale.

Properties.—Carbon monoxide is a colourless, tasteless gas, which possesses a peculiar though slight smell, and has a

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[1] Fownes, *Phil. Mag.* 1844, [3], **24**, 21.

[2] *Annalen*, 1856, **98**, 127.

[3] Wade and Panting, *Journ. Chem. Soc.* 1898, 257.

[4] Noack, *Ber.* 1883, **16**, 75.

specific gravity of 0·96716 (Rayleigh),[1] 0·96702 (Leduc).[2] The relative density remains constant up to 1200°, but at 1690° the gas partially decomposes with formation of carbon dioxide, free carbon being deposited.[3] It has been liquefied by Cailletet, Wroblewski, and Olszewski; its critical temperature is $-139°·5$, the corresponding pressure being 35·5 atmospheres, it boils at $-190°$ and solidifies at $-211°$ (Cailletet).[4] In water it is only very slightly soluble, its absorption coefficient, according to Bunsen and Pauli, being obtained from the following equation:—

$$c = 0·032874 - 0·00081632t + 0·000016421t^2.$$

It is, however, easily soluble in an acid or ammoniacal solution of cuprous chloride, Cu_2Cl_2.

Carbon monoxide burns readily in moist air with a pale blue flame forming carbon dioxide, the molecular heat of combustion being 68,000 cal. The lambent flame observed on the top of a large clear coal fire is due to the combustion of this gas.

When an electric spark is passed through a mixture of carbon monoxide and oxygen containing moisture a violent explosion occurs, but if the mixture is thoroughly dried by means of phosphorus pentoxide, the spark is no longer capable of producing an explosion.[5] The passage of powerful sparks causes the combination of the dried gases in the neighbourhood of the discharge, but the combination is not propagated through the whole of the gas.[6] The combination of the dried gases may also be brought about slowly, but completely and without flame, in contact with a heated platinum wire.[7] On addition of the slightest trace of moisture, or of substances capable of producing water, such as hydrogen, sulphuretted hydrogen, or hydrocarbons, the spark at once causes explosion, and the velocity of the explosion is increased by the addition of more water vapour up to about 4·5 per cent.[8]

The effect of moisture on the combination of carbon monoxide and oxygen may be readily shown by lighting a jet of the monoxide, previously dried with strong sulphuric acid, and then

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[1] *Proc. Roy. Soc.* 1897, **62**, 204.

[2] *Compt. Rend.* 1892, **115**, 1072.

[3] Meyer and Langer, *Ber.* 1885, **18**, 134 c.

[4] *Compt. Rend.* 1884, **99**, 706; 1885, **100**, 350; *Monatsh.* 1885, **6**, 204.

[5] Dixon, *British Association Report*, 1880, 503.

[6] Lothar Meyer, *Ber.* 1886, **19**, 1099; Beketoff, *Bull. Acad. St. Petersburg*, **2**, 175.

[7] *Phil. Trans.* 1888, A. **199**, 571.

[8] Dixon, *Phil. Trans.* 1893, A. **184**, 111.

placing over the flame a jar containing air previously shaken with the same drying agent, when the flame is immediately extinguished.[1]

A fully satisfactory explanation of these phenomena has not yet been given. It has been suggested that carbon monoxide is incapable of combining directly with oxygen, but that when moisture is present intermediate reactions take place in which the latter is concerned, with final production of carbon dioxide and regeneration of the water. Against this view is the fact that even when the gases are dried as completely as possible by all methods yet known, combination still takes place in contact with a heated platinum wire. Further, when dry cyanogen is exploded with oxygen, the first product is carbon monoxide, but in presence of excess of oxygen this is completely oxidised to the dioxide, although moisture has been as completely removed as in the case of the carbon monoxide and oxygen. It has further been shown that when a mixture of dry cyanogen and oxygen is burnt in a Smithells flame separator (p. 803), the interconal gases, consisting of nitrogen, carbon monoxide and dioxide, free from moisture, burn in the outer flame, yielding carbon dioxide and nitrogen, provided the cones are not too widely separated; in the latter case combination no longer takes place, and the outer cone is extinguished.[2]

Carbon monoxide combines directly with metallic nickel and iron to form very remarkable substances of the composition $Ni(CO)_4$ and $Fe(CO)_5$[3] (Mond). These substances readily decompose when heated into the metal and carbon monoxide. They will be described under the compounds of the metals.

Carbonic oxide is a very poisonous gas, inasmuch as it combines with the hæmoglobin of the blood: small animals die almost instantly when placed in the gas, and when even small quantities are inhaled severe headache, giddiness, and insensibility readily occur. The accidents, as well as suicides, which occur from burning charcoal in a chauffer in a small room, or from breathing air containing coal-gas, are due to the inhalation of this gas formed by incomplete combustion or contained in the coal-gas, and deaths occurring from sleeping upon lime-kilns

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[1] Traube, *Ber.* 1885, **18**, 1890.

[2] Smithells and Dent, *Journ. Chem. Soc.* 1894, 603; for a discussion of the various hypotheses suggested, see Dixon, *Journ. Chem. Soc.* 1896, 774; Armstrong, *Journ. Chem. Soc.* 1903, 1088.

[3] *Journ. Chem. Soc.* 1890, 749; 1891, 1090; *Compt. Rend.* 1891, **113**, 679; *Proc. Chem. Soc.* 1891, 126.

and brick-kilns are probably also produced by this gas. The poisonous nature of the gas from red-hot charcoal was known and expatiated upon as early as the year 1716, when F. Hoffmann published his work, *Considerations on the Fatal Effects of the Vapour from Burning Charcoal.*

The remarkable poisonous action of carbonic oxide appears to depend upon the fact that the whole dissolved and loosely combined oxygen in the blood is thereby expelled, the blood acquiring a light purple-red colour. The absorption spectrum of the carbonic-oxide-hæmoglobin is distinguished by the fact that the bands between *D* and *b* are situated nearer to *b* than is the case with oxyhæmoglobin (Hoppe-Seyler), and that, unlike the latter, it remains unchanged in presence of reducing agents. This test serves as a means of detecting cases of poisoning with the gas, and may also be employed for proving the presence of small quantities of carbon monoxide in air or other gases, which are for this purpose passed through fresh blood, and the latter then spectroscopically examined.

Traces of the monoxide in air may also be detected by shaking with a solution of palladium chloride, which is reduced to the metal if CO is present, 0·05 per cent. of the gas being thus recognisable. Ammonia and sulphuretted hydrogen must be absent, as they also reduce palladium chloride.

The quantitative estimation of the gas is carried out by explosion with oxygen, or more frequently by absorption with acid or ammoniacal cuprous chloride solution.

The composition of carbon monoxide is determined by mixing the gas with oxygen, exploding the mixture, and measuring the carbon dioxide formed. It is thus ascertained that one volume of the gas unites with half a volume of oxygen to form one volume of carbon dioxide. Now the latter is known to contain its own volume of oxygen (p. 789), and it hence follows that carbon monoxide contains half its own volume of oxygen. The molecular weight of the gas is shown by its density to be about 27·79, and this amount of it therefore contains 15·88 of oxygen and 11·91 of carbon, the formula of the gas being CO.

CARBON DIOXIDE, OR CARBONIC ANHYDRIDE, $CO_2 = 43·67$.

451 This gas belongs to the class of acid-forming oxides formerly termed acids, and is still best known under its old name

of carbonic acid. It has already been stated in the historical introduction that this gas was first distinguished from common air by Van Helmont, who termed it *gas sylvestre.* He obtained it by the action of acids on alkaline or calcareous substances, and showed that it is also formed by the combustion of charcoal, and in the fermentation and decay of carbonaceous matter, and that it likewise occurs in the mineral water at Spa, in the Grotto del Cane near Naples, and in other localities. Van Helmont describes the suffocating action it exerts on animal life as well as its effects in extinguishing flame. Fr. Hoffmann made further observations on the gas contained in effervescing mineral waters, and he states that this is frequently given off in such quantity that when the water is enclosed in bottles these are burst by the force of the gas. He also shows that this substance, to which he gave the name of *spiritus mineralis*, has the power of reddening certain blue vegetable colouring matters, and hence he considers it to be a weak acid. Although many other chemists investigated the properties of this gas, it was not until the time of Black that it was distinctly shown to differ essentially from common air. Black[1] (1755) proved that this substance is a peculiar constituent of the carbonated or mild alkalis, being, in them, combined or fixed in the solid state, whence it was termed by him *fixed air*. In the year 1774, Bergman[2] published a complete history of this peculiar air, to which he gave the name *acid of air*, because of its occurrence in the atmosphere. Its chemical nature was first properly explained by Lavoisier, who showed that, whilst mercuric oxide heated alone gives off pure oxygen gas, fixed air is evolved when it is heated with carbon, proving that this latter gas is an oxide of carbon.

Carbon dioxide is a body which is widely distributed in nature; as we have already seen, it forms a small but constant and essential constituent of the atmosphere; it is likewise invariably contained in soil, being one of the chief products of the decay of all organic substances. From the soil it is taken up by rain and spring water, and it is to this substance that the latter, to a great extent, owes its fresh and pleasant taste. It occurs in *chalybeate* and *acidulous* waters in large quantities, whilst in both ancient and modern volcanic districts it is emitted in very large volumes from the fumeroles and rents in the ground, for

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[1] *Edinb. Phys. and Literary Essays* (1755).

[2] *Opusc. I.*, 1, *De acido aëreo.*

instance in the old craters in the Eifel, at Brohl on the Rhine, as well as in the Auvergne, particularly in the neighbourhood of Vichy and Hauterive, where the gas is actually employed for the manufacture of white lead. Especially remarkable for the evolution of this gas in very large quantities is the Poison Valley in Java, which also is an old crater, and the Grotto del Cane near Naples, which is of such a construction that the heavy carbonic acid gas, entering from the fissures in the floor of the cave, at a depth of from two to three feet below the mouth of the cave, collects up to this depth, and small animals such as dogs, when thrown into the cave, respiring the impure air, fall down, whilst a man breathing the pure air above this level is unaffected by the gas.

The carbonic acid contained in the air is derived from a variety of sources; it is formed by the respiration of man and animals, as well as in the act of combustion of organised material, and in its decay and decomposition. The amount of atmospheric carbonic acid varies between certain narrow limits, but on an average reaches 3 volumes in 10,000 volumes of air. In the presence of the sunlight, plants have the power, through their leaves, of decomposing this carbonic acid, taking up the carbon to form their own tissue, and eliminating the oxygen gas; hence the amount of carbonic acid in the air does not increase beyond the limits named (Saussure).

Carbon dioxide is an acid-forming oxide giving rise to a series of salts termed the carbonates, many of which occur in nature as minerals. Amongst these is especially to be mentioned calcium carbonate, $CaCO_3$, which occurs in two distinct crystalline forms as calc-spar and arragonite, whilst it is found in a massive crystalline form in marble and limestone; calcium carbonate also forms the chief constituent of the shells of mollusca and foraminifera, the remains of which constitute the chalk formation as well as the greater part of all the limestones. The double carbonate of magnesium and calcium, $(MgCa)CO_3$, also occurs in large masses as dolomite. Amongst other naturally occurring carbonates may be mentioned magnesite, $MgCO_3$; iron spar or spathic iron ore, $(FeMnCaMg)CO_3$; witherite, $BaCO_3$; strontianite, $SrCO_3$; and calamine, $ZnCO_3$.

452 *Preparation.*—(1) In order to prepare carbon dioxide, a carbonate, such as marble or chalk, is brought into a gas-

evolution flask, and dilute hydrochloric acid poured upon it, when the gas is rapidly evolved with effervescence:—

$$CaCO_3 + 2HCl = CO_2 + CaCl_2 + H_2O.$$

The gas thus obtained invariably carries over small quantities of hydrochloric acid vapour with it, from which it may be freed by passing through a solution of sodium bicarbonate. In order to obtain a constant stream of carbon dioxide the same apparatus may be employed which was made use of for the preparation of sulphuretted hydrogen gas (Fig. 102).

(2) Another method of obtaining a constant current is to pour concentrated sulphuric acid over chalk, and add a very small quantity of water:—

$$CaCO_3 + H_2SO_4 = CO_2 + CaSO_4 + H_2O.$$

The dilute acid cannot be employed for this purpose, since the calcium sulphate formed, which is soluble in the concentrated acid, does not dissolve in the dilute acid, and thus prevents its further action on the chalk.

(3) The gas thus obtained from chalk possesses a peculiar smell, which is due to the presence of small quantities of volatile organic matter always contained in the chalk. In order to prepare a very pure gas, sodium carbonate may be decomposed with pure dilute sulphuric acid, thus:—

$$Na_2CO_3 + H_2SO_4 = CO_2 + Na_2SO_4 + H_2O.$$

(4) Carbon dioxide may be obtained on a large scale for the preparation of sodium bicarbonate, white lead, and other commercial products by "burning" limestone, or by the combustion of charcoal or coke, but the gas then always contains large volumes of nitrogen derived from the air used for combustion. In order to obtain the dioxide in comparatively pure condition from such gases on the large scale, the mixture may be passed into a concentrated solution of potassium carbonate with which carbon dioxide combines forming potassium hydrogen carbonate, $KHCO_3$. The solution of the latter evolves carbon dioxide on warming, leaving a solution of the normal carbonate, which is used again for absorbing fresh quantities of the dioxide.

453 *Properties of Carbon Dioxide.*—Carbon dioxide is a colourless gas possessing a slightly pungent smell and acid taste. It has a specific gravity of 1·52909 according to Rayleigh,[1] or of 1·52894 according to Leduc.[2] When strongly compressed it

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[1] *Proc. Roy. Soc.* 1897, **62**, 204.

[2] *Compt. Rend.* 1898, **126**, 413.

condenses to a colourless liquid, which boils at −78·2° under atmospheric pressure, the critical temperature being 31·35°, and the critical pressure 72·9 atmospheres. When the liquid is allowed to evaporate rapidly, it solidifies to a white crystalline snow-like mass, which melts at −65°, and as this is higher than the boiling point of the liquid at atmospheric pressure, the solid on exposure to the air passes directly into the gaseous form.

Carbon dioxide does not support combustion or respiration, the flame of a candle or taper being at once extinguished when plunged into the gas, whilst animals die when confined in an atmosphere of the gas, death being, however, due to suffocation owing to absence of oxygen, and not to any specific poisonous action of the dioxide, such as that which occurs with carbon monoxide. That this cannot be the case is manifest from the fact that it is constantly taken into the lungs and emitted from them. According to Berzelius, air containing 5 per cent. of carbon dioxide can be breathed without producing any serious effects, but from Angus Smith's experiments[1] it appears that when air contains only 0·20 per cent. of the gas its effect in lowering the action of the pulse is rendered evident after the respiration has been continued for about an hour. It seems therefore premature to say that the smallest increase in the normal quantity of atmospheric carbonic acid may not be hurtful in the long run, although for a short time much larger quantities may be present without any serious results.

Owing to its high specific gravity, carbon dioxide may be readily poured from one vessel to another; this fact can be strikingly exhibited by bringing a lighted taper into the vessel into which the carbon dioxide has been poured, when it will be instantly extinguished. This property is made use of to test the presence of the gas in old wells, cellars, and coal-pits, where it frequently accumulates, and is termed *choke damp*. Before the workman descends it is usual to lower down a burning candle, and thus ascertain whether the air is pure enough for respiration. Air containing 4 per cent. of carbon dioxide extinguishes a candle-flame, but it will support respiration for a short time.

454 Carbon dioxide is a very stable body, requiring for its decomposition an extremely high temperature. When passed over pieces of porcelain in a porcelain tube, heated to a temperature of from 1200° to 1300°, it decomposes to a small extent

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[1] *Air and Rain*, p. 209.

into carbon monoxide and oxygen (Deville); and the same decomposition is brought about by the electric spark (Dalton and Henry). In this way only a small portion of the gas is decomposed, as when a certain quantity of oxygen has been formed this again combines with the carbon monoxide. Under favourable circumstances the recombination of the gases, accompanied by the passage of a flame, can be actually observed to take place periodically.[1] If, however, hydrogen, or mercury, or any oxidisable body be present, the whole of the carbon dioxide is converted into monoxide (Saussure). This decomposition is best shown by allowing the electric spark to pass by means of iron poles through a measured volume of carbon dioxide; after the action is completed, the volume of carbon monoxide formed is found to be exactly equal to that of the dioxide taken, thus:—

$$2CO_2 = 2CO + O_2,$$

the oxygen being completely absorbed by the metallic iron (Buff and Hofmann). When an electric discharge is passed through the dioxide in a tube under 3–5 mm. pressure, 65–70 per cent. is decomposed into carbon monoxide and oxygen.[2]

A piece of burning magnesium wire or ribbon continues to burn when plunged into carbon dioxide, the oxide of the metal being formed and carbon liberated:—

$$CO_2 + 2Mg = 2MgO + C.$$

When carbon dioxide is passed over heated potassium or sodium, the carbonates of these metals are formed, and carbon is set free, thus:—

$$3CO_2 + 2K_2 = 2K_2CO_3 + C.$$

Liquid carbon dioxide is also attacked by the alkali metals (Gore).

Carbon dioxide is soluble in water, its solubility being represented by the following equation:—

$$c = 1·7967 - 0·07761t + 0·0016424t^2,$$

or one vol. of water at 0° dissolves 1·7967 vols. of carbon dioxide.
„ „ 5 „ 1·4497 „ „ „
„ „ 10 „ 1·1847 „ „ „
„ „ 15 „ 1·0020 „ „ „
„ „ 20 „ 0·9014 „ „ „

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[1] Hofmann, *Ber.* 1890, **23**, 3303.
[2] Collie, *Journ. Chem. Soc.* 1901, 1063.

It is more easily soluble in alcohol of specific gravity 0·792, the coefficient of solubility being given by the following equation:—

$$c = 4{\cdot}32955 - 0{\cdot}09395t + 0{\cdot}00124t^2.$$

When the pressure is much smaller than that of the atmosphere, carbon dioxide follows Dalton and Henry's law of the absorption of gases in water, but deviation is observed from this law at higher pressures, increasing gradually as the pressure is increased.

The following table shows the volume of carbon dioxide, measured at 0° and 760 mm., dissolved by one volume of water at 0° (column S), the pressure being given in the column P.[1]

P in atmospheres.	S Vols. at 0°.	$\frac{S}{P}$
1	1·797	1·797
5	8·65	1·730
10	16·03	1·603
15	21·95	1·463
20	26·65	1·332
25	30·55	1·222
30	33·74	1·124

If the law of Henry and Dalton were correct, the value of $\frac{S}{P}$ would be constant. It appears from the table that this fraction gradually decreases in value, the solubility increasing at a slower rate than the pressure.

The aqueous solution readily becomes supersaturated with the gas when the pressure on a saturated solution is lowered, but the excess of gas is liberated when the liquid is shaken or some porous substance brought into it. Thus, if a piece of porous substance like sugar or bread be brought into a liquid, such as soda-water or champagne, which has been saturated under pressure with carbon dioxide, and which has been exposed to the air for some little time, so that the effervescence due to the diminution of pressure has ceased, a strong renewal of the effervescence is observed. Water which contains a small quantity of common salt in solution dissolves carbon dioxide more easily than common water. This depends on the fact that a chemical decomposition takes place, a part of the common salt, NaCl, being converted by the carbonic acid present into sodium hydrogen carbonate, $NaHCO_3$, free hydrochloric acid, HCl, being liberated. The presence of the latter acid may easily be shown by the addition to the liquid of a small quantity of ultramarine, this substance losing its blue colour in presence of hydrochloric acid, whilst a solution either of common salt or of carbonic acid fails to act upon it.

455 *Liquid and Solid Carbon Dioxide.*—Carbon dioxide was first liquefied by Faraday, who allowed sulphuric acid to act on ammonium carbonate in a sealed bent tube (Fig. 43, p. 183), the gas being liquefied by its own pressure. Up to the time of the liquefaction of the so-called permanent gases, by Cailletet and Pictet in 1878 (p. 102), the problems connected with liquefaction and low temperatures were chiefly studied with this gas, and it was from a study of liquid carbon dioxide that Andrews was led to his discovery of the continuity of the gaseous and liquid states (p. 98).

FIG. 181.

The first preparation of liquid carbon dioxide on the large scale was carried out by Thilorier,[1] who employed the cast-iron apparatus shown in Fig. 181, the gas being formed by acting on sodium bicarbonate with sulphuric acid in one cylinder, where it was allowed to liquefy by its own pressure, and then distilled over into the second cylinder, termed the receiver. Owing to the unsuitable nature of cast-iron for such purposes, fatal explosions occurred, and a modified apparatus was therefore introduced by Mareska and Donny, shown in Fig. 182. This

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[1] *Annalen*, 1839, **30**, 122.

consisted of two leaden cylinders surrounded by a similar one of copper, and strongly hooped with wrought-iron. The generating cylinder was charged with sodium bicarbonate and sulphuric acid, the latter being placed in the small internal cylinder, and poured on to the carbonate as required by tilting the generator. After the dioxide had liquefied it was distilled over into the receiving cylinder.

Natterer,[1] of Vienna, and Bianchi, of Paris, later on constructed an apparatus in which carbon dioxide prepared in a separate vessel was compressed by means of powerful pumps into wrought-iron pear-shaped vessels, and this principle is still adopted, except that the wrought-iron vessels have now been replaced by cylinders of mild steel, which contain about 8 litres. These are chiefly filled in certain large breweries from the carbon dioxide given off during fermentation, and also from the gas evolved from certain springs such as those at Burghold on the Rhine, or from gas specially prepared in other ways (p. 781).

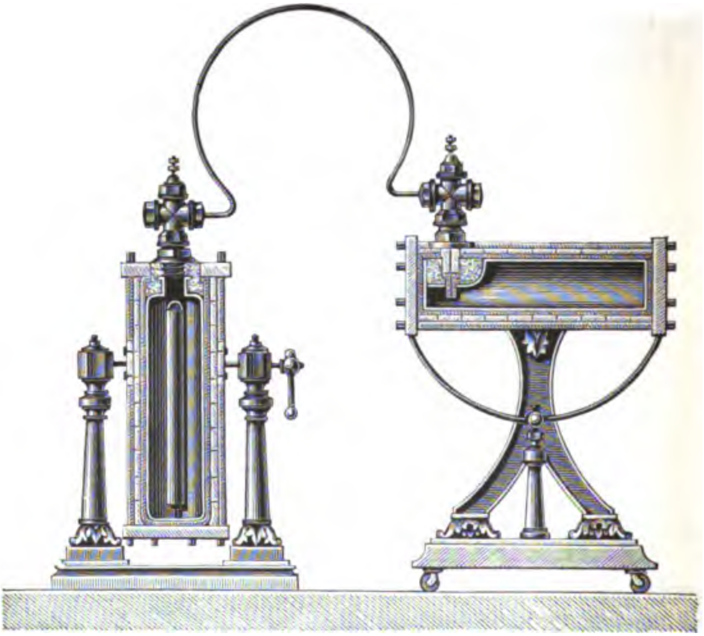

FIG. 182.

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[1] *J. pr. Chem.* 1845, **35**, 169.

It is now largely sold and used for producing cold, as well as high pressures, and is therefore employed in the manufacture of cast steel. It is also employed for beer-engines, in the manufacture of salicylic acid, and for the production of aërated waters.

Liquid carbon dioxide is a colourless, very mobile liquid, slightly soluble in water, upon the surface of which it floats. Its specific gravity is 0·9951 at –10°, 0·9470 at 0°, and 0·8266 at +20°.[1] These numbers show that liquid carbon dioxide expands more upon heating than a gas, and its coefficient of expansion is larger than that of any known body. The boiling-point of liquid carbon dioxide is –78·2° under a pressure of 760 mm., and its vapour pressure at different temperatures is given in the following table:—

Temperature.	Pressure in mm. of mercury.	Temperature.	Pressure in mm. of mercury.
–125°	5	+ 5°	30753
– 78·2	760	+15	39646
– 56·7	3876	+25	50207
– 25	13007	+35	62447
– 15	17582	+45	76314
– 5	23441		

Liquid carbon dioxide conducts electricity badly; it does not act as a solvent on most substances, does not redden dry litmus paper, and possesses no very striking chemical properties (Gore).

When the stopcock of a vessel containing liquid carbon dioxide is opened, a portion of the liquid which rushes out solidifies in the form of white snow-like flakes (Thilorier). This is caused by the absorption of heat, produced by the rapid evaporation of another portion of the liquid. For the purpose of obtaining larger quantities of this carbon dioxide snow, the apparatus shown in Figs. 183 and 184, suggested by Natterer, is employed. It consists of two brass cylinders, AB and CD, one of which can be fixed inside the other, each being fastened to a hollow non-conducting handle. The liquid carbon dioxide is allowed to pass quickly from the nozzle of the cylinder containing the liquid through the tube *d* (the position of which inside the box is shown in Fig. 184). A portion of the liquid undergoes evaporation and passes out as gas through the fine holes in the handles, whilst the larger portion remains behind as a solid finely divided crystalline bulky mass, capable of being pressed together like snow. It can also be readily prepared by

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[1] Andreef, *Annalen*, 1859. **110**, 1.

blowing liquid dioxide into a bag of coarse canvas, which retains the solid, whilst allowing the liberated gas to pass away. Solid carbon dioxide, both in the compressed and snow-like form, evaporates very slowly in the air, because of the large amount of heat of volatilisation required. Notwithstanding its excessively low temperature it may be touched without danger, the gas which it constantly emits forming a non-conducting atmosphere round it. If, however, it be pressed hard upon the skin, solid carbon dioxide produces a blister exactly like that produced by contact with a red-hot body. This snow-like mass may be readily compressed in cylindrical wooden moulds. The solid mass thus obtained has a density of about 1·2, and requires a considerable time for evaporation in the air.[1] When solid carbon dioxide is mixed with ether, and the mixture brought into a vacuum of an air-pump, the temperature sinks to −110°. A tube containing liquid carbon dioxide brought into this solidifies to a transparent ice-like solid mass (Mitchell and Faraday), the specific gravity of the ice-like solid being 1·56 at −79°.

FIGS. 183 and 184.

A process has been patented for carrying out the manufacture of solid carbonic acid by a similar method on the large scale. The solid material may be transported in bags or casks, or in the iron chamber in which it is produced.[2]

Formula of Carbon Dioxide.—It has already been shown (p. 754) that carbon dioxide is formed by the combination of

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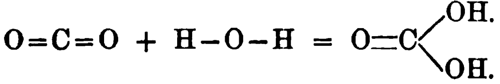
[1] Landolt, *Ber.* 1884, **17**, 309.

[2] English Patent 13, 684 (1891).

11·91 parts of carbon with 31·76 parts of oxygen. Further, when carbon burns in oxygen to form the dioxide, the volume of the latter produced is equal to that of the oxygen used, and hence one molecule of the gas must contain two atoms of oxygen, this being in agreement with the formula CO_2, in which the atomic weight of carbon is taken as 11·91.

Carbonic Acid and the Carbonates.

456 The aqueous solution of carbon dioxide contains in solution a dibasic acid, termed carbonic acid, $CO(OH)_2$. This acid does not exist in the pure concentrated state, and in this respect resembles sulphurous acid and other acids whose corresponding oxides are gaseous. Its existence is, however, proved by the fact that the aqueous solution of carbon dioxide reddens litmus paper, whereas dry carbon dioxide, whether in the gaseous or liquid state, produces no such action, and is also confirmed by the electric conductivity of the solution.[1] It has also been observed that if the water be saturated with carbon dioxide under pressure, and if the pressure be then at once removed, the gas quickly makes its escape by effervescence, the bubbles being so minute that the whole liquid, during the disengagement of the gas, appears milky. If, however, the liquid be allowed to remain in contact with the gas for some considerable time after saturation, before the pressure is removed, the gas escapes, on removal of the pressure, in large bubbles, which adhere chiefly to the sides of the glass vessel in which the liquid is contained. This difference may possibly be explained by the fact that, to begin with, the carbon dioxide is mechanically dissolved in the water, but that after remaining in contact with the water for some time a partial combination takes place between these two substances, which may be represented by the following equation :—



$$O{=}C{=}O + H{-}O{-}H = O{=}C\left\langle\begin{matrix}OH.\\OH.\end{matrix}\right.$$

A crystalline hydrate $CO_2,6H_2O$ or $H_2CO_3,5H_2O$ has been obtained by the action of CO_2 under pressure on water at low temperatures.[2]

If a current of carbon dioxide be passed through a solution

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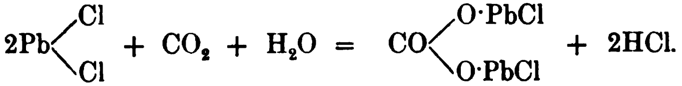
[1] Walker, *Journ. Chem. Soc.* 1900, 8; 1903, 182.

[2] Villard, *Compt. Rend.* 1894, **119**, 368.

of lead chloride, an insoluble chlorocarbonate of lead is formed[1] :—



$$2Pb\begin{cases}Cl\\Cl\end{cases} + CO_2 + H_2O = CO\begin{cases}O{\cdot}PbCl\\O{\cdot}PbCl\end{cases} + 2HCl.$$

In a similar way, when carbon dioxide is passed through a solution of common sodium phosphate, acid sodium phosphate and sodium hydrogen carbonate are formed to some extent; thus:—

$$HNa_2PO_4 + H_2CO_3 \rightleftharpoons H_2NaPO_4 + HNaCO_3.$$

Carbonic acid readily decomposes into water and carbon dioxide. In consequence of this, litmus paper, which has been turned red in the aqueous acid, becomes blue on drying. When carbon dioxide gas is passed into a solution of blue litmus, this solution becomes first violet and then of a wine-red colour; if this red solution be then heated, carbon dioxide is evolved in large bubbles, and after boiling for a few seconds the liquid again becomes blue.

Although carbonic acid itself is such an extremely unstable compound, the carbonates are very stable. Being a dibasic acid, it forms two series of salts—namely, the normal and the acid carbonates. When carbon dioxide is passed through a solution of the hydroxide of an alkali-metal, a normal carbonate is first formed ; thus:—

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$

These normal carbonates of the alkali-metals are soluble in water, and have an alkaline reaction. When they are treated with an excess of carbon dioxide, the solution becomes neutral to phenol-phthaleïn, and then contains an acid carbonate:—

$$K_2CO_3 + CO_2 + H_2O = 2HKCO_3.$$

If a solution of the hydroxides of the metals of the alkaline earths, such as lime-water or baryta-water, be treated in a similar way, a white precipitate of the normal carbonate of these metals is obtained in the first instance, these salts being almost insoluble in water, thus:—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

If more carbon dioxide gas be passed through the milky solution the precipitate dissolves, and the solution contains an acid

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[1] Hugo Müller, *Journ. Chem. Soc.* 1870, 37.

carbonate. These acid carbonates of the metals of the alkaline earths are only known in solution. When their solutions are boiled, carbon dioxide is given off, and the normal carbonate is again precipitated. All the other normal carbonates are insoluble in water. A few, such as magnesium carbonate and ferrous carbonate, dissolve like the carbonates of the alkaline earth metals in an excess of carbonic acid. Carbonic acid being a very weak acid, its salts are readily decomposed by the greater number of the acids, when the solution is not too dilute, carbon dioxide being evolved as gas. It may be readily recognised, as it produces a white precipitate when brought in contact with clear lime- or baryta-water.

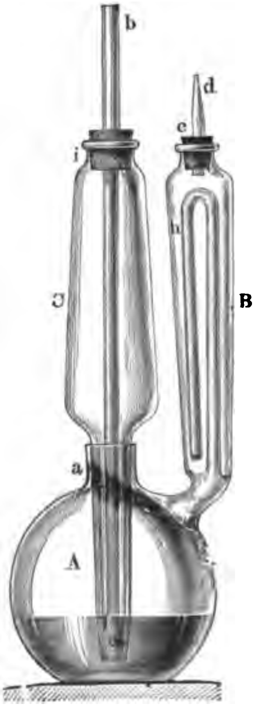

Fig. 185.

457 In order to determine the quantity of carbon dioxide contained in a carbonate, several methods may be employed. It is easy to determine this quantity by the loss of weight which the salt undergoes when an acid is added, and for this purpose the apparatus constructed by Geissler, which is thus described by Fresenius, is one of the best. The apparatus, the construction of which is shown in Fig. 185, consists of three parts, *A*, *B*, and *C*. *C* is ground into the neck of *A*, so that it may close air-tight, and yet admit of its being readily removed for the purpose of filling and emptying *A*. *b c* is a glass tube, open at both ends, and ground water-tight into *C* at the lower end, *c*; it is kept in the proper position by means of the movable cork, *i*. The cork, *e*, carries a small conducting tube *d*. The weighed substance to be decomposed is put into *A*, water is added to the extent indicated in the engraving, and the substance shaken towards the side of the flask. *C* is now filled nearly to the top with dilute nitric or hydrochloric acid, with the aid of a pipette, the cork, *i*, having been previously moved upwards without raising *b*. The cork is then again turned down, *C* again inserted into *A*, *B* somewhat more than half filled with concentrated sulphuric

acid, and *b* closed at the top, by placing over it a small piece of caoutchouc tubing with a glass rod fitted into the other end. After weighing the apparatus, the decomposition is effected by opening *b* a little and thus causing acid to pass from *C* into *A*. The carbonic acid passes through the bent tube, *h*, into the sulphuric acid, where it is dried. It then leaves the apparatus through *d*. When the decomposition is effected, *A* is gently heated, the stopper from *b* removed, and the carbon dioxide still present sucked out at *d*. The apparatus, when cold, is again weighed, and the difference between the two weighings is that of the carbon dioxide expelled.

A more accurate method consists in passing the carbon dioxide evolved by the decomposition of the substance by dilute acids through a series of drying tubes and then absorbing it in a weighed solution of potash, and thus ascertaining its weight directly.

The method for the determination of the carbon dioxide contained in the air has already been explained (p. 590).

In order to determine the quantity of this gas dissolved in water, ammonia is added to a solution of barium chloride; this is heated to the boiling point and filtered; 50cc. of this solution are then brought into a flask of 300cc. capacity, and the water under investigation added in measured quantity, the flask being again stoppered up and allowed to stand for a considerable length of time until the precipitated barium carbonate has separated out. The solution is then warmed, and the flask again stoppered. The solution is allowed to become clear, the clear liquid is poured off as completely as possible from the precipitate, the flask is filled up with water which has been well boiled, is again allowed to deposit, and the operation is repeated several times. The precipitate is then brought upon a tared filter and weighed, after being carefully dried at 110°. The quantity of carbon dioxide can be readily calculated from the weight of barium carbonate obtained.

WATER GAS.

458 At the commencement of the nineteenth century it was observed that when steam is passed over red-hot charcoal or coke a combustible gas is produced, and the latter on investigation proved to be a mixture of hydrogen with the then newly-discovered carbon monoxide and smaller quantities of

carbon dioxide. To this mixture of gases the name *water-gas* was given.

This reaction is of the highest importance from a technical point of view, inasmuch as it plays an essential part in almost all methods for the commercial production of gaseous fuel for heating purposes, and it has therefore been much studied, especially of late, both from the purely scientific and from the technical sides.

At temperatures of about 1000° the reaction between steam and carbon takes place chiefly according to the equation

$$C + H_2O = CO + H_2;$$

but some carbon dioxide is always also produced, and as the temperature falls below 1000° the proportion of dioxide formed increases, until at 600° only this latter oxide and hydrogen are produced,

$$C + 2H_2O = CO_2 + 2H_2.$$

As the reaction is chiefly used for the production of gaseous fuel, it is necessary to maintain a high temperature so as to reduce to a minimum the percentage of dioxide formed. Both of the above reactions take place with absorption of heat, the thermochemical equations being

$$C + H_2O = CO + H_2 - 27{,}724 \text{ cal.}$$
$$C + 2H_2O = CO_2 + 2H_2 - 17{,}156 \text{ cal.},$$

so that the temperature of the carbon must be maintained by heat derived from some external source, or the carbonaceous matter may be first heated by blowing in air until the mass is incandescent, steam being then passed in until the temperature falls to such an extent that the percentage of dioxide in the gas produced becomes considerable; the steam is then shut off and air again admitted, and this cycle of operations repeated.

An excess of steam must also be avoided, as otherwise the percentage of carbon dioxide is thereby much increased, inasmuch as a reversible reaction occurs between steam and carbon monoxide with formation of carbon dioxide and hydrogen,

$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$

and the lower the temperature of the gases the greater is the tendency for the production of the dioxide. The ratio

$$\frac{CO \times H_2O}{CO_2 \times H_2} = K$$

is constant at any particular temperature, and the value of the constant (K) increases with the temperature, the following values having been experimentally determined by Hahn[1]:—

t°.	K.	t°.	K.
786°	0·81	1086°	1·95
886	1·19	1205	2·10
986	1·54	1405	2·49
1005	1·68		

The technical manufacture of water-gas will be considered in the chapter on the Gas Industry.

MECHANISM OF THE COMBUSTION OF CARBON.

459 It is not yet known with certainty whether the first product of the oxidation of carbon is the monoxide or the dioxide. It was formerly supposed that carbon dioxide is always produced to begin with, and that when insufficient oxygen is present some of the carbon dioxide is acted upon by the remaining carbon with formation of the monoxide. It is, however, equally possible that the first product of the oxidation is always carbon monoxide, and that if excess of oxygen be present, this then combines with the monoxide yielding carbon dioxide. Whilst no definite experimental proof of the correctness of either hypothesis has yet been found, the work of recent investigators, and especially of Dixon and H. B. Baker, has yielded results which are more readily explained according to the second of these views than the first.

Dixon[2] has shown that, contrary to the statement of Lang,[3] carbon monoxide is always produced in small quantity together with the dioxide by the action of oxygen on carbon at 500°, although the dioxide is not reduced to the monoxide by carbon below a temperature of 600°, and it is difficult to explain the presence of carbon monoxide unless it is the primary product of oxidation. Baker[4] has further proved that thoroughly dried carbon and oxygen only combine very slowly when strongly heated, and the chief product is then the monoxide, whilst dry carbon dioxide is not reduced by dry carbon at a bright red

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[1] *Zeit. physikal. Chem.* 1903, **42**, 705; 1903, **44**, 513; 1904, **48**, 735.

[2] *Journ. Chem. Soc.* 1899, 630.

[3] *Zeit. Physikal Chem.* 1888, **2**, 62.

[4] *Phil. Trans.* 1888, **179A**, 571.

heat. These results also appear to indicate that the monoxide is first formed, and afford further evidence of the effect of traces of moisture in bringing about the combination of carbon monoxide and oxygen (p. 776). The researches of Dixon and his pupils on the explosion of gases likewise lead to the same conclusion; thus, for example, when cyanogen gas is exploded with only a sufficient quantity of oxygen to yield carbon monoxide and nitrogen, the velocity of the explosion wave is much higher than when sufficient oxygen is present for the formation of carbon dioxide. This result is readily understood if carbon monoxide is first formed in both cases, and then undergoes a second reaction before it yields the dioxide.[1]

In the formation of water-gas by the interaction of carbon and steam the same uncertainty prevails as to the nature of the primary reaction. This may take place according to the equation

$$C+2H_2O=CO_2+2H_2,$$

the dioxide being then reduced to the monoxide by the excess of carbon present, or carbon monoxide may be first formed according to the equation

$$C+H_2O=CO+H_2,$$

this gas then, in presence of excess of steam, undergoing a partial change into the dioxide and hydrogen, as already explained on p. 793. Here, again, no definite proof of either hypothesis is available, but the probabilities appear to be in favour of the primary production of carbon monoxide.

THE NATURE OF FLAME AND THE COMBUSTION OF HYDROCARBONS.

460 The first statement of the nature of flame with which we are acquainted occurs in the works of van Helmont, who regarded it as burning smoke, but scarcely recognised the part played by the atmosphere in the phenomenon. Hooke shortly afterwards speaks of "that transient shining body which we call flame" as "nothing but the parts of the oyl rarified and raised by heat into the form of a vapour or smoak, the free air that encompasseth this vapour keepeth it into a cylindrical form, and by its dissolving property preyeth upon those parts of it that

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[1] Dixon, *Journ. Chem. Soc.* 1896, 774.

are outwards . . . producing the light which we observe; but those parts which rise from the wick which are in the middle are not turned to shining flame till they rise towards the top of the cone, where the free air can reach and so dissolve them. With the help of a piece of glass anyone will plainly perceive that all the middle of the cone of flame neither shines nor burns, but only the outward superficies thereof that is contiguous to the free and unsatiated air."[1] A century later Lavoisier confirmed and extended Hooke's views, and showed that flame was due to the combination of the components of gaseous substances with the oxygen of the air, the gases being raised to incandescence by the intensity of the action.

The flames which will be first considered are those formed when a jet of combustible gas or vapour, unmixed with oxygen or inert gases, is allowed to burn in an atmosphere of air or oxygen. The simplest flames of this kind with which we are acquainted are those of hydrogen and carbon monoxide. The flame of either of these gases burning from the end of a tube appears as an incandescent cone, which on examination proves to be hollow, the incandescence only taking place when the gas has mixed with air by diffusion. The hollow nature of these, and indeed of all flames, may be readily shown in various ways. (1) A bent glass tube may be brought into the centre of the flame, when the unburnt gases will pass up the tube and may be ignited at the other end (Fig. 186). (2) The head of a match may be thrust quickly into the centre of the flame and held there for some time without the phosphorus catching fire, whilst

FIG. 186.

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[1] *Lampas*, published 1677.

the wood will be charred and may even take fire where it is in contact with the hot outer sheath of the cone. (3) A thin platinum wire held horizontally in the flame is seen to glow at two points where it comes in contact with the outer zones in which the combustion is going on, whilst between them it remains cool.

With gases which yield more than one product of combustion the phenomena become more complex. Thus, for example, the flames of cyanogen and sulphuretted hydrogen burning in air are found to consist of two sharply defined cones, possessing different colours. Matters become still more complex in the case of the flames with which we are most familiar, namely, those obtained from a burning candle or from gaseous hydrocarbons. In these flames four distinct regions, first defined by Berzelius, are usually distinguished: (*a*) the dark central region, (*b*) the yellow region, (*c*) the blue region, (*d*) the faintly luminous region, which are clearly shown in Fig. 187.

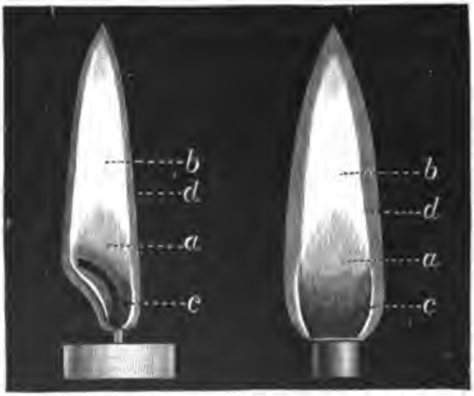

FIG. 187.

The yellow region, which is, as a rule, the largest, and gives off by far the greatest amount of light, is known in common parlance as the luminous portion. The first theory as to the cause of the great luminosity of this zone is due to Davy,[1] who believed it to be caused by the decomposition of the hydrocarbons with separation of solid particles of carbon, which increase in a high degree the intensity of the light, being raised to a very high

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[1] *On the Safety Lamp for Miners, with some Researches on Flame*, 1818; *Phil. Trans.* 1817, pp. 45 and 47.

temperature, first by the strongly heated gases around it, and then by its own combustion. Numerous facts appear to favour this view. Thus we know that the light emitted by glowing solids is much more intense than that given by glowing gases at the same temperature, as may readily be shown by holding a piece of platinum wire in the faintly luminous hydrogen flame, when it becomes heated to whiteness. Further, if we hold a sheet of paper for a short time horizontally in a candle flame a black ring of soot is deposited. Davy's theory, therefore, rapidly obtained universal acceptance, and remained unchallenged until about 1868.

About this time Frankland noticed that the flame of a candle burning on the summit of Mont Blanc emits much less light than when burning in the valley at Chamounix, although the rate of combustion is the same in both cases, and was led to examine the effect of pressure on the luminosity of flames. He found that hydrogen burns in oxygen with a luminous flame under a pressure of 20 atmospheres, and from these and other experiments [1] he concluded that dense gases and vapours become luminous at a much lower temperature than the same gases in a more rarefied condition. The luminosity of the yellow region of a hydrocarbon flame he regarded as due, not to the separation of carbon, but to the formation of dense hydrocarbons, which then burn with a luminous flame.

Further researches [2] have shown, however, that solid particles are undoubtedly present in the flame, and these must of necessity emit a large quantity of light at such a high temperature, and are the chief cause of the luminosity; but it is not unlikely that very dense hydrocarbons, when formed, likewise assist in its development.

For a long time it was generally believed, in accordance with a view apparently first promulgated by Faraday, that the separation of carbon or of dense hydrocarbon vapours is due to the preferential combination of the hydrogen of the hydrocarbons with the limited quantity of oxygen present in the yellow portion of the flame, thus causing the separation of elementary carbon or the formation of dense hydrocarbon

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[1] *Journ. Gas Lighting*, March, 1861; *Phil. Trans.* 1861, p. 629.

[2] Heumann, *Phil. Mag.* 1877, [5], **3**, 1, 89, 366; Hilgard, *Annalen*, 1854, **92**, 129; Landolt, *Pogg. Ann.* 1856, **99**, 389; Soret, *Phil. Mag.* 1875, [4], **49**, 50; Burch, *Nature*, 1884–5, **31**, 272; Stokes, *Nature*, 1891, **44**, 263; 1891–2, **45**, 133; *Proc. Chem. Soc.* 1892, 22.

vapours containing smaller percentages of hydrogen. Other observers,[1] however, showed that when hydrocarbons are burned with an insufficient supply of oxygen, the chief product is carbon monoxide, and that considerable quantities of free hydrogen are liberated. Ethylene, for example, when exploded with its own volume of oxygen, yields a mixture of carbon monoxide and hydrogen:—

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

In view of these results, the separation of carbon particles in a flame of hydrocarbon vapour burning in air cannot be regarded as due to the preferential combustion of the hydrogen, but is mainly owing to thermal changes taking place in the gas under the influence of the heat from the outer sheath of the flame. These changes take place in the dark inner cone, and finally bring about the formation of dense hydrocarbons and carbon particles, which on reaching the hotter portion of the flame become incandescent, giving the yellow luminous zone.

The thermal changes which thus occur are undoubtedly of a very complex nature, and succeed each other with such rapidity that the experimental determination of their exact nature is a matter of great difficulty. Lewes has, however, shown by the analysis of the gases taken from a coal-gas flame at different heights that the unsaturated hydrocarbons decrease very slowly in the dark portion of the flame, but quickly disappear in the luminous zone. The nature of the unsaturated hydrocarbons, however, undergoes a considerable alteration in the non-luminous zone, the amount of acetylene increasing very rapidly and forming 70 per cent. of the total unsaturated hydrocarbons when the top of the non-luminous zone is reached. He therefore concludes that the luminosity of such flames is due in the first place to the formation of acetylene by the action of heat, and that the separation of the carbon is due to the decomposition of the latter gas, which is highly endothermic, and therefore evolves heat in its decomposition, thus further increasing the temperature of the particles at the point of separation.[2] Whilst it is probable that the carbon separation

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[1] Dalton, *New System*, (1810) Part II. 442; Kersten, *J. pr. Chem.* 1861, **84**, 310; Smithells and Ingle, *Journ. Chem. Soc.* 1892, 204; Lean and Bone, *Journ. Chem. Soc.* 1892, 873.

[2] *Journ. Chem. Soc.* 1892, 322; *Proc. Roy. Soc.* 1894, **55**, 90; 1895, **57**, 394, 450.

may be in part brought about in this manner, it does not appear likely that this is the sole cause of its production.[1]

The blue portion of the flame is the least in extent of any of the four divisions, and is probably caused by the combustion of hydrocarbons which have become mixed with a sufficient quantity of air to allow them to burn with a scarcely luminous flame; it is probable that the combustion is incomplete, and that the reaction going on here corresponds with that taking place in the inner cone of the flame of the Bunsen burner (Smithells). The faintly luminous sheath is the region of complete combustion in which those substances which have been incompletely oxidised in the other portions of the flame, chiefly hydrogen and carbonic oxide, are finally converted into water and carbon dioxide. This may be regarded as corresponding with the outer cone of the Bunsen burner flame.

461 When the hydrocarbon gas or vapour is mixed with other gases before burning, the reactions which take place within the flame are greatly modified, the effect produced depending upon the nature of the added gas. Such gases may consist of (1) incombustible gases such as nitrogen and carbon dioxide; (2) combustible gases such as hydrogen and carbon monoxide; (3) supporters of combustion such as oxygen.

The effect of the addition of either of the first two classes is to reduce the luminosity, and when a sufficient percentage of the diluent gas is added the flame becomes non-luminous, the necessary percentage varying according to the gas used. Lewes gives the following table showing the volume of various gases required to render non-luminous a flame of coal-gas of 16 candle power[2]:—

1 vol. of gas requires	1·26	vol. of	carbon dioxide
„ „	2·30	„	nitrogen
„ „	5·11	„	carbon monoxide
„ „	12·4	„	hydrogen

The loss of luminosity thus brought about is due to the fact that the dilution of the hydrocarbon gas or vapour with other gases raises the temperature at which those thermal decompositions occur leading to the separation of carbon, with the result that, before a sufficiently high temperature for such separation is reached, the products come in contact with the

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[1] Smithells, *Journ. Chem. Soc.* 1895, 1049.

[2] *Journ. Chem. Soc.* 1892, 332.

air in the outer flame, and there undergo complete combustion with a non-luminous flame.[1]

The luminosity of a hydrocarbon flame, unmixed with other gases, may also be destroyed if the flame be allowed to impinge on a cold surface, the temperature of the flame being thus reduced to such an extent that in this case also no separation of carbon takes place. This phenomenon may be readily shown by placing a platinum dish containing cold water over a small coal-gas flame, when its luminosity is destroyed, but gradually reappears as the water in the dish becomes hot.

462 When the hydrocarbon gas or vapour is mixed with a gas which is a supporter of combustion, the flame produced is profoundly modified. When a sufficiently large quantity of oxygen or air is mixed with such gas the flame becomes non-luminous, and at the same time its temperature is greatly increased. Such flames have a distinctly two-coned structure, the inner cone being pale blue, whilst the outer cone is a still paler blue. The most familiar example of this type of flame, which is of the highest technical importance, is seen in the Bunsen gas burner, now so universally used for heating purposes. In this burner the gas emerges from a central jet (Fig. 189), and, passing unburnt up the tube (*e e* Fig. 188), aspirates air with it through the holes (*c d*), the mixture then

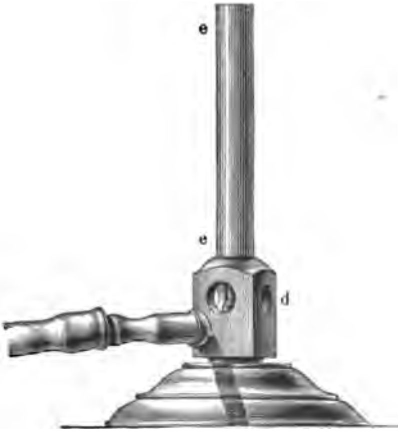

Fig. 188.

Fig. 189.

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[1] Heumann, *Annalen*, 1876, **181**, 129; 1876, **182**, 1; 1876, **183**, 102; 1876, **184**, 206; Lewes, *Journ. Chem. Soc.* 1892, 322.

burning with a pale blue or bluish, smokeless flame. If the air holes be closed, the gas burns with the usual luminous flame.

Owing to the presence of oxygen in the gas, the actions which now occur in the inner cone, under the influence of the heat from the outer sheath of flame, are quite different from those taking place in the corresponding portion of a pure hydrocarbon flame. They no longer consist simply of thermal decompositions, but of a direct combustion of the hydrocarbon with a limited supply of oxygen, forming products which are not completely oxidised, but which then burn in the outer cone on meeting the oxygen of the air, and are completely converted into carbon dioxide and steam.

463 When the quantity of air mixing with the gas in a Bunsen burner is greater than that required to destroy luminosity the mixture burns much less quietly, and the inner cone assumes a green colour; if more air be gradually added, a point is reached at which the mixture becomes so explosive that the flame passes down the tube and ignites the gas issuing from the central jet at the bottom of the burner. This continues to burn, but as it is unable at that point to obtain sufficient air for its complete combustion, large quantities of acetylene and other unsaturated hydrocarbons are formed, giving rise to the well-known unpleasant odour.

On a close examination of the phenomena which take place when air is gradually added to coal-gas or other hydrocarbon burning from the end of a glass tube, Smithells observed that the inner cone becomes greener and smaller, but that when the mixture becomes sufficiently explosive the flame does not pass down the tube as a whole, but that the green inner cone detaches itself from the outer one and passes down the tube. If the tube be constricted lower down, the descending cone is arrested at that point, the speed of the gases being there greater, and it continues to burn there whilst the outer cone remains in its former position. Smithells[1] has devised an ingenious arrangement in which this separation is readily effected, represented in Fig. 190 and 191. It consists of two concentric tubes, *a* and *b*, the former being wider than the other, and maintained in a concentric position by the india-rubber collar *c*, and the brass guide *d*. The outer tube can be slid up and down the inner one as desired. The apparatus is placed over a Bunsen burner, and on turning on the gas and

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[1] *Journ. Chem, Soc.* 1892, 204.

applying a light, the usual Bunsen flame is obtained at the top of the outer tube. If the quantity of air be now gradually increased, a point is reached at which the inner portion of the flame descends until it reaches the orifice of the inner tube, where it is arrested, the speed of the gas being greater at that point. By sliding the outer tube upwards, the two cones may be separated any desired distance, as shown in Fig. 190, or the outer tube may be lowered until the whole flame burns in the usual manner from the inner tube, as seen in Fig. 191.

When this arrangement is employed, the gases between the two cones may be readily aspirated off and analysed, and they are found to consist of carbon dioxide, carbon monoxide, steam and hydrogen, together with the nitrogen of the added air, and also sometimes small quantities of hydrocarbons. It has already been pointed out (p. 793) that when the four first named gases are present together at high temperatures (as in the manufacture of water gas) interaction occurs, and the final proportions of these constituents at any particular temperature agree with the equation

$$\frac{CO \times H_2O}{CO_2 \times H_2} = \text{constant (K)},$$

which has been found to hold also for the interconal gases (Smithells). This result has also been confirmed by Haber,[1] who has determined the composition of these gases, at various temperatures, and has shown that the results at each temperature give the same value of K as was determined by Hahn (p. 793) for the water gas equilibrium at that temperature.

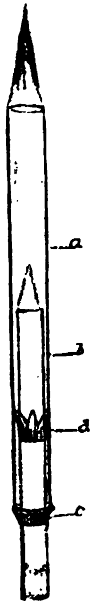

FIG. 190.

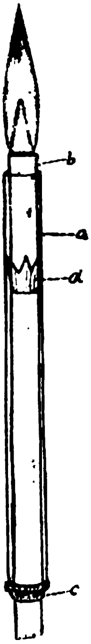

FIG. 191.

SLOW COMBUSTION OF HYDROCARBONS AT MODERATE TEMPERATURES.

464 Much light has recently been thrown on the initial reactions which take place in the oxidation of hydrocarbons by

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[1] *Journ. für Gasbeleuchtung*, 1904, 809.

the researches of Bone and his co-workers,[1] who have examined the changes which take place when simple hydrocarbons are mixed with oxygen and heated for some time at temperatures below 500°.

When a mixture of equal volumes of methane and oxygen is heated at about 450°, no preferential combustion of either carbon or hydrogen takes place, but the first recognisable products are formaldehyde and water:—

$$CH_4 + O_2 = CH_2O + H_2O;$$

the formaldehyde in presence of oxygen undergoes a further change, yielding carbon monoxide, carbon dioxide and water. Ethane, $CH_3 \cdot CH_3$, and oxygen at 250—400°, in a similar manner, yield acetaldehyde, $CH_3 \cdot CHO$, which is further acted on by oxygen forming formaldehyde, carbon monoxide, and water, the first-named then undergoing the changes already mentioned. With ozone at 100° ethane yields an appreciable quantity of ethyl alcohol, which is also probably the first product of the action of oxygen on ethane at 300°, but is so quickly oxidised to acetaldehyde at that temperature that its formation cannot then be recognised.

These results are largely in accordance with the views of Armstrong,[2] according to which the first step in the oxidation of hydrocarbons consists in the hydroxylation of the compound by the introduction of oxygen atoms between the carbon and the hydrogen. Thus with methane the initial product would be methyl alcohol, $CH_3 \cdot OH$, which by the further addition of an oxygen atom would yield methylene alcohol, $CH_2(OH)_2$. The latter compound is unknown in the free state, as it so readily splits up into formaldehyde and water, these being the products isolated by Bone. In the same way ethane, $CH_3 \cdot CH_3$, should first yield ethyl alcohol, $CH_3 \cdot CH_2OH$, and secondly the compound $CH_3 \cdot CH(OH)_2$, which at the temperature of its formation would at once split up into acetaldehyde and water, and in this case also the hypothesis has been experimentally confirmed by Bone's results.

Such reactions lead solely to the formation of carbon monoxide, carbon dioxide, and water by the gradual splitting up of the

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[1] *Journ. Chem. Soc.* 1902, 536; 1903, 1074; 1904, 693; *Proc. Chem. Soc.* 1904, 127, 202.

[2] *British Assn.* 1885; *Journ. Chem. Soc.* 1886, 112; 1895, 1122; 1903, 1088; *Proc. Roy. Soc.* 1904, **74**, 86.

oxygen compounds first formed, and do not lead to the production of elementary carbon or hydrogen or of more complex hydrocarbons. When these are obtained their formation is probably due to thermal decompositions of the various substances present under the influence of the heat evolved in the above reactions.

According to Armstrong, this or a similar series of reactions is always passed through in all cases of combustion, and even in the case of such rapid combination as takes place in the explosion of gaseous mixtures. Dixon, on the other hand, is of opinion that in the latter case, at any rate, no such complex series of reactions occurs, but that at very high temperatures direct combination takes place between carbon and hydrogen and oxygen.

According to a further hypothesis of Armstrong, this introduction of an oxygen atom between the hydrogen and the carbon atoms in the hydrocarbon is not a direct action, but the result of a series of interdependent reactions, for which the presence of water is necessary, the process being a reversal of that which takes place in the electrolysis of aqueous solutions.

GRAPHITIC ACID.

465 It has already been stated under the head of graphite that in certain properties this substance differs remarkably from the other modifications of carbon. Brodie[1] has shown that, when acted upon by certain oxidising agents, graphite is converted into a compact substance which contains oxygen and hydrogen. In order to prepare graphitic acid, an intimate mixture of one part of purified graphite and three parts of potassium chlorate is treated with so much concentrated nitric acid that the mass becomes liquid. The whole is heated for 3—4 days at 60°, and the solid residue, after washing and drying, subjected four or five times to similar treatment. It may, however, be much more quickly prepared from powdered graphite by acting on the latter with a mixture of concentrated sulphuric and nitric acids at the ordinary temperature, and gradually adding a quantity of potassium chlorate about 20 times as large as that of the graphite taken. An intermediate green coloured oxidation product is formed which is washed by

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[1] *Phil. Trans.* 1859, p. 249.

decantation, and then treated with a mixture of sulphuric acid and potassium permanganate, which completes the oxidation.[1]

Graphitic acid is thus obtained as a yellow substance, which has a crystalline appearance, but is in reality amorphous, the substance having retained the form of the original crystals of graphite. It usually contains about 42 per cent. of oxygen, and also some hydrogen, and various formulæ have been proposed for it, that given by Brodie being $C_{11}H_4O_5$. Staudenmaier[2] has, however, shown that in all probability the substance thus obtained is a mixture of compounds of very high molecular weight. On heating it undergoes an almost explosive decomposition, carbon dioxide, carbon monoxide and water being evolved, leaving a black amorphous residue, which has been termed *pyrographitic oxide,* and which is almost entirely dissolved by a mixture of potassium chlorate and nitric acid, mellitic acid, $C_6(COOH)_6$, being among the products formed. On reduction with stannous chloride, graphitic acid yields products which still contain hydrogen and oxygen, but bear the strongest physical resemblance to graphite, and are reconverted by oxidising agents into graphitic acid. These are termed by Staudenmaier *pseudographitic acids.*

The chemical nature of these products is at present very imperfectly understood. There is, however, little doubt that the graphite molecule, as well as that of the other allotropic forms of carbon, is exceedingly complex, being formed by the combination of large numbers of carbon atoms, and that the above substances are produced by the breaking up of the graphite molecule into simpler complexes under the influence of oxidising agents, yielding eventually mellitic acid, the constitution of which is known, this being a derivative of benzene, in which all six hydrogen atoms are replaced by the group COOH. On further oxidation mellitic acid is converted into oxalic acid $(COOH)_2$, and finally into carbon dioxide and water. The diamond, as already stated, is hardly attacked by oxidising agents, whilst amorphous carbon gives rise to brown soluble substances termed *humic acids,* which likewise yield mellitic acid on further oxidation.

HALOGEN DERIVATIVES OF CARBONIC ACID.

466 *Carbonyl Chloride,* $COCl_2$.—When equal volumes of dry chlorine and carbon monoxide gas are brought together in the

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[1] Staudenmaier, *Ber.* 1898, **31**, 1481; 1899, **32**, 1394, 2824.

[2] *Ber.* 1899, **32**, 2832.

dark, no action takes place, but when the mixture is exposed to light combination ensues, especially in the sunlight. J. Davy, who discovered this compound in the year 1811, termed it *phosgene* gas (from φῶς, light, and γεννάω, I give rise to). The phenomena attending the union of carbonic oxide with chlorine under the influence of light closely resemble those observed when hydrogen and chlorine combine in the light. There is a well marked period of induction,[1] which can be observed even when the gases have been carefully dried, after which the rate of combination becomes proportional to the mass of uncombined gases present.[2] Carbonyl chloride is, at the ordinary temperature, a gas possessing a peculiar, very unpleasant, pungent smell, and having a specific gravity of 3·4604 (Thomson). At a low temperature it can be condensed, forming a colourless liquid, boiling at +8°,[3] and having a specific gravity at 0° of 1·432. The compound is decomposed by water into hydrochloric acid and carbon dioxide; thus:—

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

For the purpose of preparing pure carbonyl chloride the method proposed by Wilm and Wischin[4] is the best. The mixed gases issuing at about the same rate are brought into a large glass balloon having a capacity of about ten litres; from this balloon they pass into a second one, which, like the first, is exposed to sunlight. It is best to employ a slight excess of chlorine, this being afterwards got rid of by passing the gas through a tube filled with lumps of metallic antimony. The gas thus purified can be liquefied by passing into a tube surrounded by ice, or, better, by a freezing mixture.

Carbonyl chloride is also formed when a mixture of twenty parts of chloroform, four hundred of sulphuric acid, and fifty of potassium dichromate are heated together on a water-bath (Emmerling and Lengyel), thus:—

$$\begin{gathered}2CHCl_3 + K_2Cr_2O_7 + 5H_2SO_4 = 2COCl_2 + \\ 2KHSO_4 + Cr_2(SO_4)_3 + Cl_2 + 5H_2O.\end{gathered}$$

Carbonyl chloride is also obtained when carbon tetrachloride is acted upon by fuming sulphuric acid.[5]

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[1] Dyson and Harden, *Proc. Chem. Soc.* 1893, **10**, 165: *Journ. Chem. Soc.* 1903, 201.

[2] Wildermann, *Proc Roy. Soc.* 1902, **70**, 66.

[3] Emmerling and Lengyel, *Annalen*, 1871, suppl. Band **7**, 101.

[4] *Annalen*, 1868, **147**, 147.

[5] *Ber.* 1893, **26**, 1993.

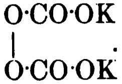
It is the chloride of carbonic acid, just as sulphuryl chloride, SO_2Cl_2, is the chloride of sulphuric acid, and when treated with ammonia is converted into the amide of carbonic acid, known as carbamide or urea, $CO(NH_2)_2$.

Carbonyl chloride is largely used in the preparation of colouring matters, for which purpose it is sometimes made by passing equal volumes of carbon monoxide and chlorine over heated animal charcoal; under these circumstances combination takes place in the dark. Carbonyl chloride is also formed by the spontaneous oxidation of chloroform when it is exposed to the light in the presence of air. Chloroform which is to be used as an anæsthetic should therefore be kept in the dark, and the bottles containing it should be kept filled, as the presence of carbonyl chloride in it renders it extremely dangerous if used for inhalation.

Carbonyl Bromide, $COBr_2$, is slowly formed by the combination of carbon monoxide and bromine vapour on exposure to light, and also by the oxidation of bromoform. It is obtained, mixed with *carbonyl chlorobromide*, COClBr, by heating carbonyl chloride with boron tribromide in sealed tubes at 150°, the two products being separated by fractional distillation. Carbonyl bromide is a colourless liquid which boils at 63—66°, and has a specific gravity of 2·48 at 0°, whilst the chlorobromide boils at 35—37° and has a specific gravity of 1·98 at 0°. Both compounds are slowly decomposed by water, and acquire a yellow colour when distilled in contact with air owing to the separation of bromine.[1]

PERCARBONIC ACID, $H_2C_2O_6$, AND THE PERCARBONATES.

467 Free percarbonic acid is unknown, but the potassium salt is formed when a concentrated solution of potassium carbonate is electrolysed at a temperature of – 10° to –15°, the ions, ·O·CO·OK, combining together to form the salt



$$\begin{array}{l}O{\cdot}CO{\cdot}OK\\ |\\ O{\cdot}CO{\cdot}OK\end{array}$$

. This separates as a bluish white amorphous powder, which is stable when dry, but rapidly decomposes when moist. On heating it loses carbon dioxide and water, and although but little affected by water at 0°, is rapidly decomposed by it at the

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[1] Besson, *Compt. Rend.* 1895, **120**, 190.

ordinary temperature, with evolution of oxygen.[1] It is a powerful oxidising agent, which on treatment with dilute acids yields a solution of hydrogen dioxide (p. 332), and is manufactured commercially for use as an oxidising agent. *Rubidium percarbonate*, $Rb_2C_2O_6$, has been prepared in a similar manner, but other carbonates are not sufficiently soluble at low temperatures to permit of their forming the corresponding percarbonates on electrolysis.

By the action of hydrogen dioxide on solutions of the carbonates, crystalline salts are obtained which, whilst acting as oxidising agents, differ in other respects from the above percarbonates. Thus sodium carbonate and hydrogen dioxide yield compounds which may be formulated as $2Na_2CO_4,3H_2O$ and $2Na_2CO_4,H_2O_2,2H_2O$, but it is as yet uncertain whether these are true salts of a percarbonic acid, or whether they are carbonates containing hydrogen dioxide in place of water of crystallisation.[2]

CARBON AND SULPHUR.

CARBON BISULPHIDE, $CS_2 = 75{\cdot}57$.

468 This compound was accidentally discovered by Lampadius in 1796, by heating pyrites with charcoal. In their investigation of carbonic oxide in the year 1802, Clément and Désormes wished to ascertain whether charcoal invariably contained combined hydrogen; they examined the action of sulphur on red-hot charcoal, and obtained the same liquid which had been previously discovered by Lampadius. This liquid they first believed to be a compound of hydrogen and sulphur, but they soon convinced themselves that it only contained carbon and sulphur. Notwithstanding these experiments, the nature of the compound remained doubtful, until Vauquelin ascertained that its vapour, passed over red-hot metallic copper, is converted into carbon and copper sulphide.

Carbon bisulphide is prepared on the large scale by passing the vapour of sulphur over red-hot charcoal. For this purpose a large upright cast-iron cylinder (Fig. 192), ten or twelve feet

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[1] Constam and v. Hansen, *Zeit. Electrochem.* 1896, **3**, 137, 445.

[2] Tanatar, *Ber.* 1899, **32**, 1544; *J. Russ. Chem. Ges.* 1902, **34**, 952; Kasensky, *J. Russ. Chem. Ges.* 1902, **34**, 202; 1903, **35**, 57.

long and one to two feet in diameter, is employed. This cylinder is placed above a furnace and surrounded by brickwork, and at the same time it is provided with a lid to admit of the whole being filled with charcoal. A second opening (*a*), furnished with a hopper, exists at the bottom of the cylinder, and this serves to bring the sulphur into the apparatus. The sulphur evaporates, and in the state of vapour combines with the red-hot carbon, impure carbon bisulphide distilling over by the tube (*c*), and collecting in the vessel (*d*) under water. The tubes (*e*) serve as condensers, to separate the vapour of carbon bisulphide from sulphuretted hydrogen formed during the reaction, owing to the presence of hydrogen in the charcoal, the sulphuretted hydrogen being absorbed by passing over the layers of slaked lime contained in the purifier (*f*). In actual work the yield of bisulphide is about 20 per cent. below the theoretical amount. The crude substance invariably contains sulphur in solution, from which, however, it may be separated by distillation; but other sulphur compounds, which impart to the crude material a most offensive odour, are also contained in the distillate. In order to remove these impurities, different processes are in use. The substance was formerly purified by frequent re-distillation over oil or fat, by which means the disagreeably smelling compounds were held back. Another means of purification employed is that of shaking the liquid with mercury, and allowing it to remain for a long time in contact with corrosive sublimate in the cold, and then distilling it off white wax.

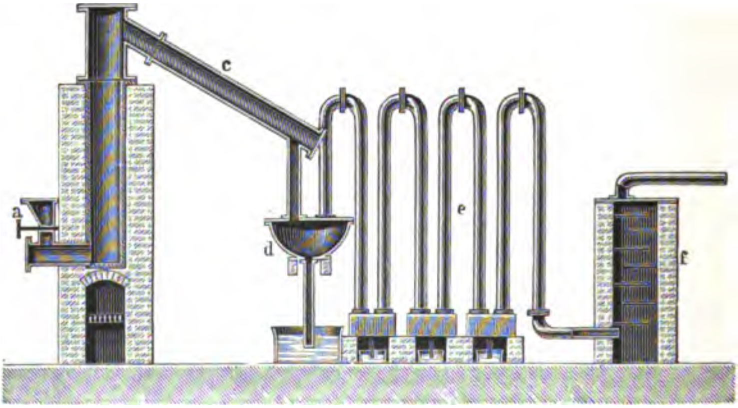

FIG. 192.

Pure carbon bisulphide is a colourless, mobile, strongly refracting liquid, possessing a sweetish smell not unlike that of ether or chloroform, having a specific gravity at 0° of 1·29232 (Thorpe) and boiling at 46°. It solidifies at −116°, remelting at −110° (Wroblewski and Olszewski). When carbon combines with sulphur to form carbon bisulphide, heat is absorbed which is given out again when it is decomposed. Like many substances of this class it is decomposed into its elements when the vapour is subjected to the shock caused by the explosion of fulminate of mercury, but at atmospheric pressure the decomposition is only local and is not transmitted through the whole mass of the vapour.

Carbon bisulphide is very inflammable and burns in the air, forming carbon dioxide and sulphur dioxide. The combination with oxygen takes place slowly below the temperature of ignition, a slight phosphorescence being observed, and as usual in such cases the exact temperature of ignition varies, but it occurs immediately at temperatures above 260°. The vapour of carbon bisulphide when mixed with oxygen can be exploded by a spark even when the mixture is thoroughly dried, differing in this respect from carbon monoxide. With excess of oxygen a mixture of carbon dioxide, sulphur dioxide, and trioxide, and sometimes free sulphur is produced, carbon monoxide, carbonyl sulphide, and unaltered carbon bisulphide being also present in the explosion wave. With an insufficient quantity of oxygen, the products are carbon dioxide and monoxide, sulphur dioxide, carbonyl sulphide and unaltered carbon bisulphide, but in no case is free carbon formed, and it is therefore improbable that the vapour is dissociated into its elements before combining with oxygen.

When a mixture of the vapour and air is burnt in a Smithells separator (p. 803), the interconal gases consist of nearly equal volumes of carbon monoxide and sulphur dioxide, together with small quantities of carbon dioxide, carbonyl sulphide, sulphur vapour and unaltered carbon bisulphide.[1]

A mixture of the vapour of carbon bisulphide and nitric oxide burns with a very bright blue flame, particularly rich in chemically active rays. Carbon bisulphide is powerfully poisonous, and its vapour soon produces fatal effects on small animals exposed to its action. It not only acts as a poison when inhaled in large quantity, but it produces very serious

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[1] Dixon and Russell, *Journ. Chem. Soc.* 1899, 600.

effects upon the nervous system when inhaled for a considerable time even in very small amount.

The vapour of carbon bisulphide acts as a powerful antiputrescent, and Zöller[1] has shown that meat and other putrescible bodies may be preserved fresh for a long time if kept in an atmosphere containing the vapour of this compound.

Carbon bisulphide is only slightly soluble in water, 1000 c.c. of the latter dissolving 1·74 c.c. of bisulphide at 22°, whilst at the same temperature 1000 c.c. of carbon bisulphide dissolve 9·74 c.c. of water.[2] It is largely used in the arts, especially in the indiarubber and woollen manufactures, in the first case as a solvent for the caoutchouc, and in the second as a means of regaining the oil and fats with which the wool has been treated. As it dissolves iodine in large quantity, but does not dissolve appreciably in water, it is employed for the purpose of determining the amount of moisture contained in commercial iodine. A remarkably characteristic reaction of carbon bisulphide is that it possesses the power of combining with triethylphosphine, $P(C_2H_5)_3$, a derivative of common alcohol, to form a solid compound crystallising in magnificent red crystals, and having the composition $P(C_2H_5)_3CS_2$. It is absorbed by alcoholic potash with formation of potassium xanthate $KS{\cdot}CS{\cdot}OC_2H_5$.

Many attempts have been made to prepare carbon monosulphide, CS, corresponding to carbon monoxide. This was stated by Deniger[3] to be produced as a gas by heating a mixture of chloroform and sodium sulphide, or of iodoform and silver sulphide, in a sealed tube, but Russell and Smith[4] have been unable to confirm these results. According to Thomsen[5] it is obtained mixed with nitrogen by repeatedly passing the latter gas saturated with carbon bisulphide vapour over heated copper.

Other compounds of carbon and sulphur have been described, but these consist for the most part of amorphous brown substances, and are probably mixtures. A compound *tricarbon disulphide*, C_3S_2, has been described by Lengyel,[6] who prepared it by passing the vapour of carbon bisulphide over an electric arc passing between carbon poles. It is a deep-red liquid,

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[1] *Ber.* 1877, **10**, 707.

[2] Herz, *Ber.* 1898, **31**, 2669.

[3] *J. pr. Chem.* 1895, [2], **51**, 346.

[4] *Journ. Chem. Soc.* 1902, 1528.

[5] *Zeit. anorg. Chem.* 1903, **34**, 187.

[6] *Ber.* 1893, **26**, 2960.

which is slowly volatile at the ordinary temperature, the vapour causing a copious flow of tears. It distils partly unchanged under diminished pressure, but is partly converted at the same time into a black solid amorphous modification of the same composition. It combines with bromine to form a yellow compound of the composition $C_3S_2Br_6$, which has a not unpleasant aromatic smell.

THIOCARBONIC ACID, H_2CS_3.

469 The salts of this acid, which is sometimes termed sulphocarbonic acid, are formed by processes analogous to those by which the carbonates are produced. This is shown by the reaction, discovered by Berzelius, in which carbon bisulphide is brought in contact with a solution of the sulphide of an alkali-metal; thus:—

$$CS_2 + Na_2S = Na_2CS_3,$$

corresponding to

$$CO_2 + Na_2O = Na_2CO_3.$$

When alcohol is added to a solution thus obtained, the thiocarbonate separates out in the form of a heavy liquid of a brownish-yellow colour. On addition of cold dilute hydrochloric acid, free *thiocarbonic acid* separates as a yellow oil, possessing a most disagreeable penetrating odour; when slightly heated, it is resolved into carbon bisulphide and sulphuretted hydrogen.

The thiocarbonates of the alkali-metals and those of the alkaline earths are soluble in water.

The soluble thiocarbonates give a brown precipitate with copper salts, a yellow precipitate with dilute silver nitrate solution, and a red precipitate on the addition of a lead salt. These precipitates rapidly become black, owing to the formation of the corresponding sulphides.

Perthiocarbonates.—Carbon bisulphide combines with sodium and potassium bisulphides much more readily than with the monosulphides, yielding salts of the composition Na_2CS_4, which are also obtained by treating the thiocarbonates with sulphur.[1]

THIOCARBONYL CHLORIDE, $CSCl_2 = 114{\cdot}1$.

470 This compound was obtained by Kolbe[2] by acting for some weeks with dry chlorine gas upon carbon bisulphide.

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[1] Gélis, *Compt. Rend.* 1875, **81**, 282.

[2] *Annalen*, 1843, **45**, 41.

According to Carius,[1] it can be easily obtained by heating phosphorus pentachloride and carbon bisulphide together in sealed tubes at 100°, when the following decomposition takes place:—

$$PCl_5 + CS_2 = PSCl_3 + CSCl_2.$$

It is most readily obtained by acting on the compound $CSCl_4$ described below, with tin and hydrochloric acid, and forms a strongly smelling liquid which boils at 73·5°, has a specific gravity of 1·5085 at 15°, and is only slowly attacked by water.[2]

The compound $CSCl_4$ is obtained by the action of chlorine on carbon bisulphide in presence of a little iodine, and is a most unpleasant-smelling liquid, boiling with slight decomposition at 149°.

CARBONYL SULPHIDE OR CARBON OXYSULPHIDE, $COS = 59·55$.

471 This gas, discovered by Than,[3] is formed when a mixture of sulphur vapour and carbon monoxide is passed through a moderately heated tube. It is also obtained by numerous other reactions, such, for example, as the action of sulphur trioxide[4] or chlorosulphonic acid[5] on carbon bisulphide. It is usually prepared by the action of dilute acids on potassium thiocyanate, the thiocyanic acid first formed splitting up into carbonyl sulphide and ammonia:—

$$HCNS + H_2O = COS + NH_3,$$

the latter combining with the excess of acid present. To obtain the pure gas the following method is employed:—

To a cold mixture of five volumes of sulphuric acid and four volumes of water such a quantity of potassium thiocyanate is added that the mass just remains liquid. The evolution of gas, which commences without heating, is regulated either by cooling or gently warming the mixture, and with care a constant current of gas can thus be obtained. The decomposition which takes place is as follows:—

$$NCSK + H_2O + 2H_2SO_4 = COS + KHSO_4 + (NH_4)HSO_4.$$

The gas invariably contains the vapours of hydrocyanic acid, HCN, and bisulphide of carbon, and is purified by passing

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[1] *Annalen*, 1859, **112**, 193.

[2] Klason, *Ber.* 1887, **20**, 2378.

[3] *Annalen Suppl.* 1867, **5**, 236.

[4] Armstrong, *Ber.* 1869, **2**, 712.

[5] Dewar and Cranston, *Zeitsch. Chem.* 1869, **5**, 734.

through strong alkali (1 part in 2 of water), concentrated sulphuric acid, and finally through a mixture of triethylphosphine, benzene, and pyridine, and may be further purified by liquefaction.[1]

Carbonyl sulphide is a colourless gas, having a specific gravity of 2·1046, and a peculiar resinous smell, which at the same time resembles that of sulphuretted hydrogen. It becomes liquid at 0° under a pressure of 12·5 atmospheres, the liquid boiling at $-47°$ under atmospheric pressure and solidifying when poured out. The critical temperature is 105° and the critical pressure 60 atmospheres. It is very inflammable, taking fire even when brought in contact with a red-hot splinter of wood, and burning with a blue slightly luminous flame. A mixture of one volume of the gas with one and a half volumes of oxygen inflames with slight explosion, burning with a bright blue flame; if, however, it be mixed with seven volumes of air, the mixture burns without explosion. When quite dry a mixture of the gas with oxygen is not exploded by the passage of a spark. A platinum wire heated to whiteness by the electric current decomposes the gas completely, without alteration of volume, into sulphur and carbon monoxide. Carbonyl sulphide is soluble in water; one volume of water dissolves 0·8 volume of the gas at 13·5°, and imparts to the solution its own peculiar smell and taste. The sulphur-waters of Harkány and Parád in Hungary possess similar properties, and probably contain, as other sulphur waters may do, carbonyl sulphide. The aqueous solution gradually decomposes with formation of sulphuretted hydrogen and carbon dioxide thus:—

$$COS + H_2O = SH_2 + CO_2.$$

The gas is quickly absorbed by aqueous solutions of caustic alkalis containing 1 part of alkali to 4 parts of water, with formation of a carbonate and a sulphide:—

$$COS + 4KOH = K_2CO_3 + K_2S + 2H_2O.$$

Stronger alkali only dissolves it slowly, but it is rapidly absorbed by alcoholic potash.

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[1] Hempel, *Zeit. angew. Chem.* 1901, **14**, 865.

CARBON AND NITROGEN.

Cyanogen Compounds.

472 The history of these compounds commences with the discovery of Prussian blue, made accidentally early in the eighteenth century by a colour-maker of the name of Diesbach. The fact was shortly afterwards communicated to the alchemist Dippel, who ascertained the conditions under which the formation of the colouring matter takes place. The method for preparing the colour was, however, first published by Woodward, who states that it was obtained by calcining the alkali obtained by heating equal parts of cream of tartar and saltpetre with ox-blood. The residue of the calcination was then lixiviated, and green vitriol and alum added to the solution, whereby a greenish precipitate was thrown down, which, on treatment with hydrochloric acid, yielded the blue colour.[1] About the same time John Brown found that animal flesh could be employed instead of blood, and Geoffroy, in 1725, showed that other animal matters could be used for the same purpose.

Up to this time very remarkable opinions were held concerning the composition of this colouring matter. Geoffroy, for example, assumed that the colour was due to metallic iron which, owing to the presence of the alum, was in an extremely fine state of division. In 1752, Macquer found that Prussian blue could be manufactured without the use of alum, and that, when the colouring matter is boiled with an alkali, oxide of iron remains behind, and a peculiar body is formed which is found in solution. To this substance (known later as prussiate of potash and now termed potassium ferrocyanide) the name of phlogisticated potash was given, and it was believed that the iron contained in the Prussian blue was coloured blue by a peculiar combustible substance. During the years 1782–5, Scheele occupied himself with the investigation of this compound, and he showed that when phlogisticated potash is distilled with sulphuric acid a very volatile and inflammable body is formed, which is soluble in water, and possesses the property, when treated with alkalis and green vitriol, of forming a very beautiful blue colour. To this body

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[1] *Phil. Trans.* 1724.

the name of prussic acid was given. In 1787 the investigation of this compound was taken up by Berthollet, who proved that iron was contained in the prussiate of potash as an essential constituent, together with alkali and prussic acid; and that prussic acid, the salts of which yield ammonia and carbonic acid as products of decomposition, consists of carbon, nitrogen, and hydrogen. These results were afterwards confirmed by the investigations of other chemists, but it is especially to the labours of Gay-Lussac that we owe a clear statement of the true composition of this acid and its salts. His researches are of great theoretical interest, as it is in them that we find the fact, for the first time, clearly pointed out, that a compound substance may exist which is capable of acting in many respects as if it were an element. Gay-Lussac[1] showed in 1811 that prussic acid is a compound consisting of hydrogen combined with a radical containing carbon and nitrogen, to which he gave the name of *cyanogène* (from *κύανος*, dark blue, and *γεννάω*, I produce). He proved, moreover, that the salts obtained by the action of prussic acid upon a base are compounds of this *cyanogène* with metals. In corroboration of this view, in 1815 he was able to show that this radical cyanogen can be prepared and is capable of existing in the free state.

By the name of *compound radical* we signify a group of atoms which plays the part of a single atom, or, employing Liebig's classical definition, we may say that cyanogen is a radical because

(1) "It is a never-varying constituent in a series of compounds:

(2) "It can be replaced in these compounds by other simple bodies:

(3) "In its compounds with a simple body, this latter may be easily separated or replaced by equivalent quantities of other simple bodies."

"Of these three chief and characteristic conditions of a compound radical, at least two must be fulfilled if the substance is to be regarded as a true compound radical."[2]

In addition to cyanogen, a number of other compound radicals are known, some of which have already been mentioned. These radicals are distinguished one from another, as the elements are, by their quantivalence. Thus, nitrogen peroxide, NO_2, is a monad radical occurring in nitric acid and in many of its

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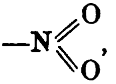
[1] *Annales de Chimie*, 1811, **77**, 128; 1815, **95**, 136.

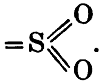
[2] *Annalen*, 1838, **25**, 3.

derivatives, and to it the name of nitroxyl has been given. Its constitution is represented as follows:—

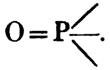


indicating that the two atoms of dyad oxygen are connected with the nitrogen each by two of the combining units of the pentad atom of the latter. Hence, one combining unit of the nitrogen remains free, and the group acts consequently as a monad radical.

Sulphur dioxide or sulphuryl, SO_2, serves as an instance of a dyad radical. This radical is contained in sulphuric acid and a large number of compounds derived from it. It is termed a dyad because, of the six combining units of the sulphur atom, four only are saturated by combination within the molecule, and its constitution may, therefore, be represented by the following formula:—



Many phosphorus compounds contain a triad radical, phosphoryl, PO, which, however, like the greater number of radicals, is not known in the free state. It contains the pentad phosphorus atom combined with the dyad oxygen atom, and its constitution can be represented as follows:—



Cyanogen, CN, is a monad radical, as it contains the triad atom of nitrogen and the tetrad atom of carbon; its constitution is represented thus:—

$$N{\equiv}C{-}.$$

The radical cyanogen, to which the symbol Cy, instead of the formula CN, is sometimes given, combines like chlorine with hydrogen and the metals, and its compounds may, therefore, be compared with those of chlorine, to which they have the strongest resemblance in their physical and chemical properties:—

Hydrocyanic acid, CyH.	Hydrochloric acid, ClH.
Potassium cyanide, CyK.	Potassium chloride, ClK.
Potassium cyanate, CyOK.	Potassium hypochlorite, ClOK.
Free cyanogen, Cy_2.	Free chlorine, Cl_2.

Cyanogen derivatives are formed in a number of ways, but, until the last decade of the nineteenth century, practically the whole of the cyanides of commerce were obtained by a method differing but little from that employed in 1725. This consists in heating together a mixture of potassium carbonate, iron, and nitrogenous matter, which results in the formation of potassium ferrocyanide, K_4FeCy_6, mixed with a number of other substances from which it is readily separated in a pure state owing to the facility with which it crystallises. This compound and Prussian blue, formed from it by the action of iron salts, were largely employed in the dyeing and calico-printing industries; and the ferrocyanide was also converted into potassium cyanide, which was used in the electroplating of gold and silver.

Other methods of formation of cyanides were, however, observed. Thus, whereas carbon and nitrogen do not when alone combine directly at high temperatures, they do so in presence of an alkali: when nitrogen, for example, is passed over a strongly heated mixture of carbon and potash, potassium cyanide is formed; or if potash is replaced by baryta, the corresponding barium cyanide is produced:—

$$N_2+4C+K_2CO_3=2KCN+3CO.$$
$$N_2+3C+BaO=Ba(CN)_2+CO.$$

Hydrocyanic acid is also produced in small quantity when ammonia is passed over heated charcoal, and it is probable that the hydrocyanic acid found in crude coal-gas and the blast-furnace gases is, in part at any rate, formed in this manner.

The introduction, in 1887, of the McArthur-Forrest process for the extraction of gold by means of potassium cyanide solution brought about a largely increased demand for cyanides, and since then many new and more economical methods of production have been developed, so that the old method so long practised has now been superseded. Much of the cyanide of commerce is now obtained from the hydrocyanic acid in crude coal-gas (*see* later), and it is also largely produced synthetically from the nitrogen of the air or from ammonia. The final product is in most cases potassium or sodium cyanide, or a mixture of both salts. (Such details as are known concerning the manufacture will be considered in Vol. II.)

CYANOGEN GAS, OR DICYANOGEN, C_2N_2 or Cy_2.

473 This gas, which was discovered by Gay-Lussac, is formed when the cyanides of mercury, silver, or gold are heated. For this purpose it is usual to employ mercuric cyanide, which decomposes thus:—

$$Hg(CN)_2 = Hg + C_2N_2.$$

The mercury salt, placed in a tube of hard glass fitted with a cork and gas-delivery tube, or in a small hard glass retort, is heated to dull redness, and the gas collected over mercury.

The heat of formation of mercuric cyanide is large, and a very high temperature is therefore required to bring about this decomposition. If mercuric chloride be mixed with the cyanide, the cyanogen comes off at a lower temperature, as the mercury then combines with the mercuric chloride forming mercurous chloride, and the whole reaction, represented by the equation

$$Hg(CN)_2 + HgCl_2 = (CN)_2 + 2HgCl,$$

takes place with slight evolution of heat.

Cyanogen gas can also be obtained by other reactions. For instance, it is formed when ammonium oxalate is heated with phosphorus pentachloride; thus:—

$$C_2O_4(NH_4)_2 = C_2N_2 + 4H_2O.$$

It is also formed by gently igniting an intimate mixture of two parts of well-dried potassium ferrocyanide, $Fe(CN)_6K_4$, with three parts of mercuric chloride.[1] According to Berzelius, however, the gas thus prepared contains free nitrogen, and he recommends the employment of potassium cyanide in place of the ferrocyanide. There is no doubt that in this reaction mercuric cyanide is first obtained, and this is then decomposed as already described.

Cyanogen is most readily obtained by gradually adding a concentrated solution of potassium cyanide to a solution of two parts of crystallised copper sulphate in four parts of water, and then warming; cyanogen is evolved and cuprous cyanide simultaneously separates out from the solution. If the cuprous cyanide be washed by decantation, and then treated with ferric chloride, the remainder of the cyanogen is evolved.[2]

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[1] Kemp, *Phil. Mag.* 1843, [3], **23**, 179.

[2] Jacquemin *Ann. Chim. Phys.* 1886, [6], **6**, 140.

Cyanogen gas is found in small quantities in the gases proceeding from the blast furnaces,[1] and it is likewise formed when a mixture of ammonia and coal-gas is burnt in a Bunsen burner. The following equation probably explains the reaction which takes place in the latter case:—

$$4CO + 4NH_3 + O_2 = 2C_2N_2 + 6H_2O.$$

Cyanogen is a colourless gas possessing a peculiar pungent odour resembling that of peach kernels. It is poisonous, and burns, when ignited in air, with a characteristic purple-mantled flame, with formation of carbon dioxide and nitrogen. A mixture of equal volumes of cyanogen and oxygen, dried as completely as possible, is exploded by passing an electric spark, with formation of carbon monoxide and nitrogen, whereas the dioxide is produced from a mixture of one volume of cyanogen and two of oxygen.[2] (*See also* p. 795.)

$$C_2N_2 + O_2 = 2CO + N_2.$$
$$C_2N_2 + 2O_2 = 2CO_2 + N_2.$$

Cyanogen is decomposed when subjected to the action of electric sparks, carbon being deposited, and small quantities of paracyanogen formed.

The specific gravity of the gas is 1·806 (Gay-Lussac); when exposed to pressure or to cold, cyanogen condenses to a colourless liquid which boils at −20·7°, and possesses at 17° a specific gravity of 0·866. The critical temperature is 124°, and the critical pressure 61·7 atmospheres. When cooled to a still lower temperature the liquid freezes, forming a crystalline mass which melts at −34·4°.[3] According to Bunsen[4] the vapour pressure of liquid cyanogen at different temperatures is as follows:—

Temperature.	Pressure in atmospheres.
−20·7°	1
−10	1·85
0	2·7
+10	3·8
15	4·4
20	5·0

At the ordinary atmospheric temperature, one volume of

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[1] *J. pr. Chem.* 1847, [1], **42**, 145.

[2] Dixon, Strange, and Graham, *Journ. Chem. Soc.* 1896, 759.

[3] Davy and Faraday, *Phil. Trans.* 1823, 196.

[4] *Pogg. Ann.* 1839, **46**, 101.

cyanogen dissolves in four volumes of water, and in twenty-three volumes of alcohol. The aqueous solution soon becomes turbid, with separation of a brown powder known as *azulmic acid*, and the solution contains ammonium oxalate together with smaller quantities of ammonium carbonate, hydrocyanic acid, and urea (Wöhler). The formation of these products of decomposition will be explained later (Vol. III., Part ii., 2nd edition, pp. 139, 343). Cyanogen gas when passed over heated potassium unites directly with the metal, forming potassium cyanide.

Paracyanogen, $(CN)_n$.—In the preparation of cyanogen from mercuric cyanide a brown powder remains behind. This substance possesses the same percentage composition as cyanogen, but its molecular weight is unknown; when it is heated in a current of carbon dioxide or nitrogen it gradually volatilises, being converted into cyanogen gas.

HYDROCYANIC ACID, OR PRUSSIC ACID,[1] HCN.

474 We owe the discovery of hydrocyanic acid to Scheele in 1782. It was subsequently examined by Ittner,[2] and by Gay-Lussac, the latter of these chemists preparing it for the first time in the anhydrous condition.[3] For this purpose he heated mercuric cyanide with hydrochloric acid in a flask, leading the gas, which was evolved, through a long tube half-filled with pieces of marble in order to retain any vapours of hydrochloric acid which might be carried over, the second half of the tube being filled with chloride of calcium for the purpose of absorbing any aqueous vapour. The gas, thus dried, was passed into a receiver placed in a freezing mixture, where it was condensed. According to this method only two-thirds of the theoretical amount of acid is obtained, as the mercuric chloride unites with a portion of the prussic acid to form a compound which is decomposed only at a high temperature. If, however, ammonium chloride be added, this salt combines with the mercuric chloride, and the whole of the hydrocyanic acid is set free.[4]

Pure hydrocyanic acid is also obtained by leading sulphuretted hydrogen gas over dry mercuric cyanide heated to about

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[1] The name *acide prussique* was first used by Guyton de Morveau.

[2] *Beiträge z. Geschichte d. Blausaüre*, 1809.

[3] *Ann. Chim.* 1811, **78**, 128, and 1815, **95**, 136.

[4] Bussy and Buignet, *Ann. Chim. Phys.* 1864, [4], **3**, 232.

30°. The salt is placed in a long horizontal tube of which the front portion is filled with lead carbonate for the purpose of retaining the excess of sulphuretted hydrogen; as soon as this begins to turn black the evolution of sulphuretted hydrogen is stopped.

Hydrocyanic acid is generally prepared from potassium ferrocyanide, which, as Scheele showed, is decomposed by dilute sulphuric acid. A process described by Wöhler enables us to prepare any desired quantity, either of the aqueous acid of different strengths, or of the anhydrous compound. A cold mixture of 14 parts of water and 7 parts of concentrated sulphuric acid is poured upon 10 parts of coarsely powdered potassium ferrocyanide contained in a large retort the neck of which is placed upwards in a slanting direction. If the anhydrous acid be required, the vapour is allowed to pass through cylinders or U-tubes filled with calcium chloride and surrounded by water heated to 30°, after which the gas, thus dried, is condensed by passing into a receiver surrounded by ice or a freezing mixture. To prepare the aqueous acid the drying apparatus may be omitted and the gas evolved from a flask as shown in Fig. 193, passed through a Liebig's condenser, and then led into the requisite quantity of distilled water. The action of the dilute sulphuric acid upon potassium ferrocyanide is represented by the following equation:—

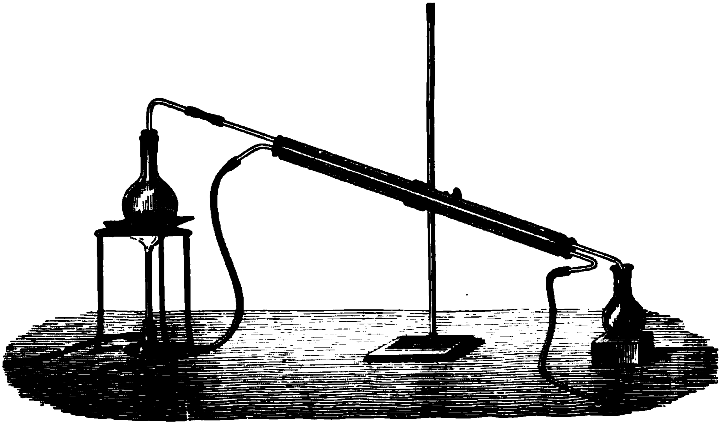

FIG. 193.

$$2Fe(CN)_6K_4 + 3H_2SO_4 = 3K_2SO_4 + Fe(CN)_6K_2Fe + 6HCN.$$

As is seen from this equation, only half of the cyanogen contained in the ferrocyanide is obtained as hydrocyanic acid, but notwithstanding this loss the method is simpler and cheaper than those previously described. Now that 98 per cent. potassium cyanide can be cheaply purchased, this may be employed in place of the ferrocyanide, a mixture of equal volumes of sulphuric acid and water being allowed to drop on to lump cyanide in a flask.[1]

Amongst the various other methods which have been described for the preparation of this acid, one proposed by Clarke may be mentioned, inasmuch as by this method a dilute acid may readily be prepared having an approximately known strength. For this purpose nine parts of tartaric acid are dissolved in sixty parts of water and the solution poured into a flask so that it is nearly filled. Four parts of potassium cyanide are then added, and the flask closed by means of a cork. The mixture is then well shaken, and allowed to stand for some time until the whole of the cream of tartar (acid tartrate of potassium) has separated out, after which the dilute hydrocyanic acid is poured off. This should contain 3·6 per cent. of hydrocyanic acid, and only a small amount of cream of tartar in solution, the reaction being represented by the following equation:—

$$KCN + C_4H_6O_6 = HCN + C_4H_5KO_6.$$

Hydrocyanic acid is also formed when a series of electric sparks is passed through a mixture of acetylene and nitrogen;[2] thus:—

$$C_2H_2 + N_2 = 2HCN.$$

It is also obtained by the passage of the silent discharge through a mixture of cyanogen and hydrogen.[3]

475 *Properties.*—Pure anhydrous hydrocyanic acid is a colourless very mobile liquid possessing a characteristic smell resembling that of bitter almonds, and producing when inhaled in small quantities a peculiar irritation of the throat. Its specific gravity is 0·7058 at 7° and 0·6969 at 18° (Gay-Lussac); it boils at 26·1°, and forms a colourless vapour which possesses the specific gravity 0·944 at 19°. At −15° the liquid solidifies to a mass of colourless feathery crystals. If a drop of the liquid acid be brought on a glass rod into the air, evaporation takes place so quickly,

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[1] Wade and Panting, *Journ. Chem. Soc.* 1898, 255.

[2] Berthelot, *Compt. Rend.* 1873, **77**, 1141.

[3] Boillot, *Compt. Rend.* 1873, **76**, 1132.

and so much heat is thereby absorbed, that a portion of the liquid freezes. Hydrocyanic acid is miscible in all proportions with water, alcohol, and ether. A very singular phenomenon is observed when hydrocyanic acid is mixed with water, inasmuch as a diminution of temperature occurs without any increase of the volume of the liquid; on the contrary, a diminution of volume takes place, and this is the greatest when equal volumes of water and acid are mixed. In this mixture the proportions correspond to the relations, $3H_2O+2HCN$, and, in this case, the diminution in bulk which occurs is from 100 to 94 (Bussy and Buignet). The anhydrous acid as well as its concentrated aqueous solution is easily inflammable, and burns with a beautiful violet flame. When not absolutely pure, it decomposes very readily on exposure to light, with separation of a brown substance, and formation of ammonia, whilst, in the case of the pure dilute acid, formic acid, ammonia, and other bodies are produced. The tendency to decomposition is much diminished by the presence of traces of mineral acid or of formic acid. Concentrated mineral acids, as well as boiling alkalis, decompose hydrocyanic acid into ammonia and formic acid, water being taken up; thus:—

$$HCN+2H_2O=NH_3+H.CO.OH.$$

On the other hand, hydrocyanic acid and water are formed when the ammonium salt of formic acid is quickly heated.

Pure hydrocyanic acid is one of the most powerful and rapid of known poisons. When a small quantity of the vapour of the pure substance is drawn into the lungs instant death ensues; small quantities produce headache, giddiness, nausea, dyspnœa, and palpitation.

A few drops brought into the eye of a dog kill it in thirty seconds, whilst an internal dose of 0·05 grain is usually sufficient to produce fatal effects upon the human subject, but cases have been known in which 0·1 grain has been taken without death ensuing. As antidotes, ammonia and chlorine water have been proposed, and these appear to be efficacious, although we are unable to explain their mode of action, for ammonia under ordinary conditions only forms ammonium cyanide, and chlorine cyanogen chloride, both of which are bodies as poisonous as prussic acid itself. Hydrocyanic acid is used as a medicine, and is a constituent of several officinal preparations, such as laurel water, bitter-almond water, &c., which are obtained by distilling the leaves of the common laurel, or bitter almonds with water.

These plants do not contain the acid ready formed; but, in common with most of the plants of the same family, contain *amygdalin*, a complicated compound which, under certain circumstances, splits up into sugar, oil of bitter almonds, and hydrocyanic acid.

476 To estimate the quantity of hydrocyanic acid contained in these preparations, an excess of potash solution is added to a measured or weighed quantity of the liquid, and then by means of a burette a solution of nitrate of silver containing 6·3 grams in one litre is dropped in until a permanent precipitate appears. Each cc. corresponds to two milligrams of anhydrous hydrocyanic acid. In this reaction the double cyanide, $AgCN + KCN$, is formed, which is not decomposed by alkalis, and is soluble in water. Hence as soon as exactly half the quantity of hydrocyanic acid present is converted into silver cyanide, one drop more of the silver solution will produce a permanent precipitate of silver cyanide.[1]

To detect hydrocyanic acid, as in cases of poisoning, the suspected matter is acidulated with tartaric acid, and the acid distilled off. The distillate is made alkaline with caustic soda, and a mixture of a ferrous and ferric salt (a solution of ferrous sulphate oxidised by exposure to the air) is added, and then an excess of hydrochloric acid. Prussian blue remains undissolved if hydrocyanic acid be present; if the quantity contained be very small, the solution appears first of a green colour, and, on standing, deposits dark blue flakes. When dilute hydrocyanic acid is mixed with yellow ammonium sulphide, and the liquid evaporated to dryness over a water-bath, ammonium thiocyanate is formed. The presence of this body is made known by means of ferric chloride, which produces in a solution of thiocyanate a deep blood-red coloration.[2]

THE CYANIDES.

477 Hydrocyanic acid turns blue litmus paper red, but it is so weak an acid that its soluble salts are decomposed by the carbonic acid of the air, and are partially hydrolysed by water, so that they smell of hydrocyanic acid, and have an alkaline reaction even when their solution contains excess of hydrocyanic acid.

The cyanides of the alkali metals, and those of the metals of

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[1] Liebig, *Annalen*, 1849, **71**, 102.

[2] *Ibid.* 1847, **61**, 127.

the alkaline earths, are soluble in water, and are also poisonous. The cyanides of the other metals, with the exception of mercuric cyanide, are insoluble in water. They dissolve, however, in the cyanides of the alkali metals, with the formation of soluble double cyanides. These double cyanides may be divided into two distinct classes. The compounds of the first class are easily decomposed by dilute acids with the formation of an insoluble metallic cyanide, and free hydrocyanic acid; and possess all the usual properties of the cyanides; of these, silver-potassium cyanide and nickel-potassium cyanide may serve as examples.

$$AgCN.KCN + HNO_3 = AgCN + HCN + KNO_3.$$
$$Ni(CN)_2.2KCN + 2HCl = Ni(CN)_2 + 2HCN + 2KCl.$$

The double cyanides of the second class, although containing, like the others, two different metals, possess wholly distinct properties. The best known of these are the yellow prussiate of potash or potassium ferrocyanide, $Fe(CN)_2.4KCN$, and the red prussiate of potash or potassium ferricyanide, $Fe(CN)_3.3KCN$. If to a solution of the first of these salts dilute hydrochloric acid be added, no hydrocyanic acid is evolved, but a white crystalline precipitate is obtained having the composition $H_4Fe(CN)_6$. This compound is a powerful acid, to which the name of *ferrocyanic acid* has been given, and in which the four atoms of hydrogen can be either partially or wholly replaced by metals. In the same way the potassium can also be replaced in the red prussiate of potash by hydrogen, and thus *ferricyanic acid*, $H_3Fe(CN)_6$, can be obtained.

Similar double compounds are known, especially those of cobalt, manganese, platinum, and of the metals allied to it. In these compounds the second metal does not act as a base, but has combined with the cyanogen to form an acid radical, for example, $Fe(CN)_6$, which then unites with hydrogen and metals in the same manner as other acid radicals such as chlorine. (See also Vol. II., under Iron.)

478 *Detection and estimation of cyanogen and the cyanides.*—The detection of cyanogen in the cyanides, such as those of the alkalis and alkaline earths, which are easily decomposed by dilute acid, is simple enough. If the solution is not already alkaline, a solution of caustic soda is added, and next, a few drops of a solution of ferrous sulphate (green vitriol) which has been partially oxidised by exposure to the air; an excess of hydro-

chloric acid is then added, when a precipitate of Prussian blue is thrown down. In this reaction the ferrous salt in the presence of caustic soda and a cyanide gives rise to the formation of sodium ferrocyanide, which then undergoes the usual reaction with the ferric salt which is present. Cyanides, which do not evolve hydrocyanic acid on the addition of a dilute acid, may be decomposed by fusing them with dry sodium carbonate. The fused mass is then dissolved in water, and the filtered liquid treated according to the above-mentioned process.

In the soluble cyanides, as well as in those which are decomposed by dilute acids, the quantity of cyanogen can readily be determined by precipitation with silver nitrate. A precipitate of silver cyanide is obtained, which, after washing and drying at 110°, is weighed. This method, however, cannot be employed in the cases of mercuric cyanide, potassium ferrocyanide, and analogous substances, in which cases it is necessary to obtain hydrocyanic acid from the compound by some appropriate method, such as treatment with sulphuretted hydrogen, distillation with dilute sulphuric acid, &c. Concerning the further details of the qualitative and quantitative analysis of such compounds we must refer to treatises on analytical chemistry.

COMPOUNDS OF CYANOGEN WITH THE ELEMENTS OF THE CHLORINE GROUP.

479 *Cyanogen Chloride*, ClCN.—Berthollet obtained this compound in 1787 by the action of chlorine on hydrocyanic acid, and believed it to be oxygenated hydrocyanic acid. Its true composition was recognised by Gay-Lussac in the year 1815. According to Wöhler, this compound is easily obtained by passing chlorine gas into a saturated aqueous solution of mercuric cyanide containing some of the solid salt, until the liquid is saturated with the gas, and the air which remains above the liquid is replaced by chlorine. The vessel is then well closed and placed in a dark room till all the mercuric chloride has dissolved, or all the chlorine has combined. In order to remove any free chlorine which may remain the solution is shaken up with mercury, and the liquid heated in order to expel the cyanogen chloride, the volatile product being condensed by passing through a bent tube plunged into a freezing mixture.

Great care must be exercised when preparing the compound in this manner, as explosions frequently occur.[1]

According to Gautier[2] the liquid chloride is best obtained by leading chlorine into a mixture of one part of hydrocyanic acid and four parts of water contained in a retort or flask which is connected with an inverted Liebig's condenser. As soon as the liquid has attained a green colour, the current of chlorine is stopped, and an excess of mercuric oxide and calcium chloride is added to the liquid, which is well cooled down in a freezing mixture. The cyanogen chloride is next distilled off and condensed in a well-cooled receiver.

At the ordinary temperature cyanogen chloride is a gas which has a very penetrating odour, and causes a copious flow of tears; it is very readily condensed to a liquid, and freezes at −18°, forming colourless prisms, which according to Regnault[3] melt at −7°, the liquid formed boiling at 12·7°, whilst according to Würtz[4] it melts at −12 to −15° and boils at 15·5°. Its vapour density is 2·13. When allowed to stand it is partially converted into the polymeric cyanuric chloride $C_3N_3Cl_3$.

Cyanogen Bromide, CNBr.—This compound, which was discovered in the year 1827 by Serullas,[5] is formed by the action of bromine on hydrocyanic acid, or on the metallic cyanides. If bromine is added drop by drop to a well-cooled aqueous solution of potassium cyanide, crystals separate out, which consist of a mixture of cyanogen bromide and potassium bromide.[6] When these crystals are heated to a temperature of from 60° to 65°, cyanogen bromide sublimes in the form of delicate transparent prisms, which soon pass into the cubical form. It melts at 52° and boils at 61·3° under 750 mm. pressure,[7] has an exceedingly pungent smell, and acts very powerfully upon the eyes. It is also poisonous; one grain dissolved in a small quantity of water brought into the œsophagus of a rabbit produced instant death (Serullas). According to Bineau the specific gravity of its vapour is 3·607. When not absolutely pure, cyanogen bromide is converted at 130° to 140° into *cyanuric bromide*, $C_3N_3Br_3$.[8]

Cyanogen Iodide, CNI.—This compound was discovered by

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[1] Weith, *Ber.* 1874, **7**, 1745.

[2] *Bull. Soc. Chim.* 1865, [2], **4**, 5.

[3] *Jahresb.* 1863, 70.

[4] *Annalen*, 1851, **79**, 284.

[5] *Ann. Chim. Phys.* 1827, **34**, 100.

[6] Langlois, *Ann. Chim. Phys.* 1861 [3], **61**, 482.

[7] Mulder, *Rec. Trav. Chim.* 1886, **4**, 151; 1886, **5**, 85.

[8] Eghis, *Zeitsch. Chem.* 1869, **5**, 376; Ponamarew, *Ber.* 1885, **18**, 3261.

Davy in the year 1816,[1] and is easily formed by the action of iodine on mercury cyanide and other metallic cyanides, whilst it frequently occurs as an impurity in commercial iodine. According to Liebig it can be best obtained by dissolving iodine in a warm concentrated solution of potassium cyanide until the liquid solidifies on cooling to a crystalline mass. Cyanogen iodide forms long delicate white needles, easily soluble in alcohol and ether, and from these solutions the compound crystallises in four-sided tablets. It is sparingly soluble in water. It melts at 146·5°, but begins to volatilise at a much lower temperature. It has a smell similar to that of the bromide, and is equally poisonous.

CYANIC ACID, NCOH.

480 Cyanic acid was first observed by Vauquelin in the year 1818, although it was first distinctly recognised as a peculiar acid and its properties more exactly investigated by Wöhler in 1822. Its salts are formed when cyanogen gas is led into an alkali; thus:—

$$C_2N_2 + 2KOH = CNOK + CNK + H_2O.$$

When potassium cyanide is melted in the presence of air, or better, with the addition of an easily reducible oxide or peroxide such as red lead, potassium cyanate is formed.

The most convenient method of preparing the cyanates is by the action of potassium bichromate on potassium ferrocyanide. For this purpose 200 grams of completely dehydrated potassium ferrocyanide are mixed whilst still warm with 150 grams of fused potassium bichromate, and the whole heated in an iron dish. The black product is then quickly extracted with a mixture of 800 cc. of 80 per cent. ethyl alcohol and 100 cc. of methyl alcohol, potassium cyanate separating from the filtrate on cooling.[2]

Cyanates are readily decomposed by dilute acids, but the cyanic acid at the same time takes up water, carbon dioxide and ammonia being formed. Therefore on adding a dilute acid to potassium cyanate effervescence takes place, carbon dioxide being given off. This has a pungent smell, due to the presence of a trace of cyanic acid. By acting on a cyanate with dry

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[1] *Gilb. Ann.* **54**, 384.

[2] Bell, *Chem. News*, 1875, **32**, 49; Erdmann, *Ber.* 1893, **26**, 2438.

hydrochloric acid, cyanic acid is set free. It at once combines, however, with hydrochloric acid to form the compound HCl, NCOH, a colourless liquid, fuming in the air. It is impossible to isolate cyanic acid from this compound, because it at once changes into the polymeric cyanuric acid $C_3N_3(OH)_3$.

The only reaction by which cyanic acid can be obtained is by the decomposition of cyanuric acid by heat, when it is resolved into three molecules of cyanic acid, the vapour of which must be condensed by means of a freezing mixture. Cyanic acid is a colourless mobile liquid having a most pungent smell. On taking the vessel containing it out of the freezing mixture the liquid soon becomes turbid and hot, and is soon converted with a crackling noise, or if in large quantity with explosive ebullition, into a white porcelain-like mass which is a polymeric modification, called *cyamelide*, the molecular weight of which is unknown. On heating, cyamelide is reconverted into cyanic acid.

Of the cyanates the most interesting salt is the *ammonium cyanate*, $NCO(NH_4)$, obtained as a white crystalline mass by mixing the vapour of dry cyanic acid with dry ammonia. The freshly prepared aqueous solution gives the reactions of a cyanate and of ammonia, but on standing for some time, or on heating, the ammonium cyanate is transformed into the isomeric *carbamide* or *urea*, $CO(NH_2)_2$. The dry salt also undergoes the same transformation on heating, and the change may also be shown by heating a solution of potassium cyanate to which an equivalent quantity of ammonium sulphate has been added.

THIOCYANIC ACID, NCSH.

481 This acid, to which the name of *sulphocyanic acid* has also been given, was mentioned by Bucholz in 1798, but first carefully examined by Porret in 1808. He obtained its potassium salt by boiling a solution of potassium sulphide with Prussian blue. Its quantitative composition was ascertained by Berzelius in 1820.[1]

Salts of this acid are formed by the direct union of sulphur with a cyanide. Thus, for instance, potassium thiocyanate is easily obtained by melting together potassium cyanide and

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[1] *Schweig. Journ.* 1820, **31**, 42.

sulphur or dried potassium ferrocyanide with potassium carbonate and sulphur. The ammonium salt is obtained by warming hydrocyanic acid with yellow sulphide of ammonium; thus:—

$$\left.\begin{matrix}NH_4\\NH_4\end{matrix}\right\}S_2+HCN=\left.\begin{matrix}NH_4\\H\end{matrix}\right\}S+NH_4SCN.$$

It is commercially obtained from crude coal-gas in this manner.

Ammonium thiocyanate is easily obtained by warming a mixture of concentrated alcoholic ammonia and bisulphide of carbon which has been allowed to stand for a considerable time. Ammonium thiocarbonate and thiocarbamate are formed, and these are decomposed on heating, with evolution of sulphuretted hydrogen (Millon); thus:—

$$CS\left\{\begin{matrix}SNH_4\\SNH_4\end{matrix}\right.=NCS{\cdot}NH_4+2H_2S.$$

$$CS\left\{\begin{matrix}NH_2\\SNH_4\end{matrix}\right.=NCS{\cdot}NH_4+H_2S.$$

For this purpose it is best to take 350—400 grams of carbon bisulphide, 600 grams of 95 per cent. alcohol, and 800 grams of ammonia (sp. gr. 0·912). As soon as the carbon bisulphide has dissolved, the solution is concentrated, and on cooling the salt separates out in crystals.[1] If a solution of mercuric nitrate be added to a solution of ammonium or potassium thiocyanate, a heavy white precipitate of mercuric thiocyanate, $(CNS)_2Hg$, is thrown down. This substance when dry is easily inflammable, and burns with a pale sulphur flame, leaving a very voluminous residue behind. This salt is used for the preparation of the so-called Pharaoh's Serpents.

Aqueous thiocyanic acid may be readily obtained by decomposing barium thiocyanate with dilute sulphuric acid. This solution may be distilled under diminished pressure, the acid coming over with the first portion, and if dried over calcium chloride forms a yellowish oil which decomposes,[2] yielding a yellow amorphous substance termed *perthiocyanic acid*, which has the empirical formula $C_2H_2N_2S_3$, but has probably a much higher molecular formula.[3] On boiling the aqueous solution, the greater part of the acid is converted with absorption of water into carbonyl sulphide

[1] Claus, *Annalen*, 1875, **179**, 112.

[2] Klason, *J. pr. Chem.* 1887, [2], **36**, 57.

[3] Chattaway and Stevens, *Journ. Chem. Soc.* 1897, 607, 833.

and ammonia, whilst at the same time some hydrocyanic acid is formed. Thiocyanic acid and its soluble salts are coloured blood-red by ferric chloride, ferric thiocyanate being formed. The soluble thiocyanates produce with silver nitrate a precipitate of silver thiocyanate which is insoluble even in presence of the stronger acids. A solution of potassium or ammonium thiocyanate of known strength is, therefore, used for the purpose of determining the quantity of silver contained in a solution, by adding some nitric acid and ferric sulphate and then dropping in a standard solution of ammonium thiocyanate from a burette until the formation of a slight red colour shows that all the silver has been thrown down.[1] In a similar manner thiocyanates may be estimated with a standard solution of silver nitrate.

CYANOGEN SULPHIDE, OR THIOCYANIC ANHYDRIDE, $(CN)_2S$.

482 In order to prepare this compound, silver thiocyanate is added to an ethereal solution of cyanogen iodide, the solution evaporated, and the residue treated with hot carbon bisulphide.[2] If the solution be cooled to 0°, cyanogen sulphide separates in rhombic tablets, which possess a smell like that of cyanogen iodide. They melt at 60°, but begin to volatilise when heated above 30°. They are very soluble in water, alcohol, and ether, and are decomposed by caustic alkalis as follows:—

$$\left.\begin{matrix}CN\\CN\end{matrix}\right\}S+2\left.\begin{matrix}K\\H\end{matrix}\right\}O=\left.\begin{matrix}CN\\K\end{matrix}\right\}S+\left.\begin{matrix}CN\\K\end{matrix}\right\}O+H_2O.$$

Cyanogen Selenide, $(CN)_2Se$, is obtained by adding dry silver cyanide to a solution of selenium bromide in carbon bisulphide. It crystallises in tablets, which are decomposed by water into selenium, selenious acid, and hydrocyanic acid.[3]

CYANAMIDE, $CN.NH_2$.

483 This body was discovered by Bineau,[4] who prepared it by the action of dry ammonia on gaseous cyanogen chloride.

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[1] Volhard, *J. pr. Chem.* 1874, [2], **9**, 217.

[2] Linnemann, *Annalen*, 1849, **70**, 36.

[3] Schneider, *Pogg. Ann.* 1866, **129**, 364.

[4] *Ann. Chim. Phys.* 1838, [2], **67**, 368; 1839, [2], **70**, 251.

The solid mass thus obtained was supposed by him to be the chloride of cyanammonium, $ClCN(NH_3)$, but Clöez and Cannizzaro[1] showed in 1851 that this substance consists of a mixture of ammonium chloride and cyanamide :—

$$2\,N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + CNCl = NH_4Cl + N\left\{\begin{matrix}CN\\H\\H\end{matrix}\right.$$

Cyanamide is most readily obtained, however, by the action of mercuric oxide upon a cold, not too dilute, solution of thio-urea[2] :—

$$CS(NH_2)_2 + HgO = CN(NH_2) + HgS + H_2O.$$

The mercuric oxide must be very finely levigated, or a dense precipitated oxide may be employed; this is suspended in water and gradually added to the solution of thio-urea; an excess of the oxide must most carefully be avoided. The end of the reaction may be easily recognised, a drop of the solution being brought on to filter paper, and then a drop of ammoniacal silver solution added; this produces a black spot as long as thio-urea is present. As soon as all the thio-urea has been decomposed the solution is filtered and evaporated down on a water-bath, and the residue treated with ether; on evaporation of the ethereal solution, pure cyanamide is left behind. It forms small colourless crystals, melting at 40°, which deliquesce on exposure to the air, and are volatile with steam. If a few drops of nitric acid be added to its solution, cyanamide is transformed into urea :—

$$CN.NH_2 + H_2O = CO(NH_2)_2.$$

Cyanamide acts as a weak base; the *hydrochloride* $CN.NH_2, 2HCl$ is readily obtained as a crystalline powder when hydrochloric acid gas is passed into a solution of cyanamide in anhydrous ether (Drechsel). The hydrogen of the cyanamide may also be replaced by metals; thus, for instance, if an ammoniacal silver solution be added to an aqueous solution of cyanamide, an amorphous yellow precipitate, $CN.NAg_2$, is thrown down, which crystallises from hot ammonia in microscopic needles. In the same way, if one part of sodium be

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[1] *Compt. Rend.* 1851, **32**, 62.

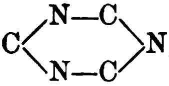
[2] Volhard, *J. pr. Chem.* 1874, [2], **9**, 6; and Drechsel, *J. pr. Chem.* 1874, [2], **9**, 284.

dissolved in 15 parts of absolute alcohol, and an alcoholic solution of cyanamide added to the cold liquid, a light crystalline powder falls down, possessing, according to Drechsel, the composition CN.NHNa.

Calcium Cyanamide $(CN.NH)_2Ca$ is formed when lime and carbon are heated in the electric furnace in presence of nitrogen, and is now employed on the large scale for the manufacture of cyanides and as a manure.[1]

When cyanamide is strongly heated it undergoes polymerisation, first forming dicyanamide, $C_2N_4H_4$, and finally cyanuramide, $C_3N_6H_6$.[2]

POLYMERISATION OF CYANOGEN COMPOUNDS.

484 Mention has frequently been made of the fact that many of the cyanogen derivatives readily undergo polymerisation—that is, are converted into compounds having the same percentage composition but a higher molecular weight. Thus cyanogen chloride readily passes into *cyanuric chloride* $C_3N_3Cl_3$, cyanic acid into *cyanuric acid* $C_3N_3(OH)_3$, and cyanamide into *dicyanamide* $C_2N_4H_4$ and *cyanuramide* $C_3N_6H_6$. These compounds have very different properties from the cyanogen derivatives from which they are produced, and contain in most cases a nucleus of carbon and nitrogen atoms united together in such a manner as to form a closed chain. Thus the cyanuric compounds all contain the nucleus , and from them other substances containing the same nucleus can be prepared. The sulphocyanides also yield compounds containing closed chains of carbon, nitrogen and sulphur atoms. All these substances and many other complex derivatives of carbonic acid and cyanogen are usually considered under the head of Organic Chemistry.

CARBAMIC ACID. $CO\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$.

485 This acid, the monamide of carbonic acid, is not known in the free state, although we are acquainted with its salts and its ethereal salts. Ammonium carbamate is formed when dry

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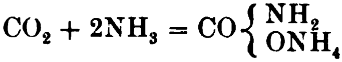
[1] Engl. Patent, 16,298, 1902.

[2] Haag, *Annalen*, 1862, **122**, 22.

carbon dioxide is brought into contact with dry ammonia (J. Davy, H. Rose):—



$$CO_2 + 2NH_3 = CO\begin{cases} NH_2 \\ ONH_4 \end{cases}.$$

It is best prepared by passing a rapid stream of the two gases into well-cooled absolute alcohol. A deliquescent crystalline powder is formed, which smells of ammonia, and is readily soluble in water.[1] Ammonium carbamate is also contained in the commercial carbonate of ammonia, and can be obtained from this source by allowing the commercial substance to stand in contact with saturated aqueous ammonia for forty hours at a temperature of from 20° to 25°; on cooling, the carbamate separates out. The specific gravity of the vapour of ammonium carbamate between 37° and 100° is 0·892 (Naumann); hence it appears that this body is completely dissociated on evaporation into carbon dioxide and ammonia. If the gaseous mixture thus obtained be allowed to cool, ammonium carbamate is again formed, but only slowly, owing to the fact that the combination is not a direct one, an intramolecular change taking place.[2] When brought in contact with acids, ammonium carbamate evolves carbon dioxide, whilst with alkalis it evolves ammonia.

The *sodium* and *potassium* salts have also been prepared, and also a *calcium* salt which has probably the constitution

$$CO\begin{cases} NH_2 \\ O.Ca(OH). \end{cases}$$

CARBAMIDE OR UREA, $CO(NH_2)_2$.

486 Urea, which is largely contained in urine and in other liquids of the animal body, was first described in the year 1773 by H. M. Rouelle as *Extractum saponaceum urinæ.* It was, however, more accurately investigated in the year 1790 by Fourcroy and Vauquelin. The discovery by Wöhler, in the year 1828,[3] that when an aqueous solution of ammonium cyanate is heated, this compound undergoes a molecular change and is converted into urea, is one of the most important discoveries of modern chemistry, inasmuch as it was the first case in which a compound

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[1] Basarow, *J. pr. Chem.* 1870, [2], **1**, 283; Mente, *Annalen*, 1888, **248**, 234.

[2] Naumann, *Annalen*, 1869, **150**, 1.

[3] Wöhler, *Pogg. Ann.* 1828, **12**, 253.

formed in the animal body was prepared from its inorganic constituents:—

$$NC(ONH_4) = CO(NH_2)_2.$$

Urea is also obtained by the action of ammonia on carbonyl chloride[1]:—

$$COCl_2 + 2NH_3 = CO(NH_2)_2 + 2HCl.$$

It was obtained first in this manner mixed with ammonium chloride, by John Davy, in 1812, sixteen years before Wöhler's synthesis, but he did not recognise its identity, although he determined the relative volumes of the gases entering into combination.[2]

It is likewise produced by heating ammonium carbamate or common carbonate of ammonia to a temperature of from 130° to 140° (Basarow):—

$$CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right. = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + H_2O.$$

Urea is found in the urine of all mammalia, especially that of the carnivora, and also in small quantities in that of birds and reptiles, as well as in the excreta of the lower animals. It forms an important constituent of the vitreous humour of the eye, and invariably occurs in small quantity in blood, and sometimes in perspiration and pus. In order to prepare urea from the urine the liquid is evaporated down on a water-bath to dryness, the residue treated with alcohol, the alcoholic solution evaporated, and the residue again treated with absolute alcohol. On evaporating this last solution, urea, slightly coloured with extractive matter, remains behind.

A second method is to evaporate down urine to a syrupy consistency, and then add pure nitric acid, when urea nitrate separates out as a crystalline powder, which is decomposed on the addition of potassium carbonate, with formation of potassium nitrate and free urea. These bodies can then be easily separated by treatment with alcohol, in which the urea dissolves. A third method is that recommended by Berzelius: a concentrated solution of oxalic acid is added to the evaporated urine, when a precipitate of the insoluble oxalate of urea is thrown down; this is boiled with chalk, when the pure urea is left in solution.

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[1] Natanson, *Annalen*, 1856, **98**, 287; Neubauer, *Annalen*, 1857, **101**, 342.

[2] *Phil. Trans.* 1812; see also Matthews, *Chem. News*, 1890, **62**, 364.

The preparation of urea from ammonium cyanate is, however, by far the best. For this purpose potassium cyanate is first prepared by heating dried potassium ferrocyanide with potassium bichromate in the manner described on p. 830. This may be then dissolved in water, and an equivalent quantity of ammonium sulphate added, or the requisite quantity of the latter may be added to the mother liquors obtained in preparing the cyanate. Potassium sulphate is formed, the greater part of which crystallises out, the small portion still remaining in solution being got rid of by evaporation and subsequent crystallisation. The liquid is then evaporated to dryness, and the urea contained in the dry residue is extracted with boiling alcohol, and may be further purified by recrystallisation from amyl alcohol.[1]

The change of ammonium cyanate into urea is a reversible one, and on heating urea and water at 100° about 4·4 per cent. is converted into ammonium cyanate,[2] which then partially decomposes yielding ammonia.[3]

Urea dissolves in its own weight of cold water and in every proportion in boiling water. It also dissolves in five parts of cold and one part of boiling alcohol, but is almost insoluble in ether. It crystallises in long striated quadratic prisms, and possesses a cooling taste resembling that of nitre. On heating, it melts at 132°, and decomposes when heated to a higher temperature. Although urea does not possess an alkaline reaction, it combines easily with acids, and forms a series of salts which crystallise well, and of which the following are the most important:—

Urea Hydrochloride, $CO(NH_2)_2HCl$.—This salt is formed when dry hydrochloric acid acts upon urea. In consequence of the heat which is evolved in the act of combination, the compound appears in the form of a yellowish oil, but this crystallises on cooling. On addition of water it is resolved into its constituents.

Urea Nitrate, $CO(NH_2)_2NO_3H$.—This is a very characteristic compound, being soluble in water but almost insoluble in nitric acid. Hence if pure nitric acid be added to a tolerably concentrated solution of urea, a crystalline precipitate falls, which on recrystallisation from solution in hot water is deposited in prismatic crystals.

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[1] Erdmann, *Ber.* 1893, **26**, 2438.

[2] Walker and Hambly, *Journ. Chem. Soc.*, 1895, 746.

[3] Fawsitt, *Zeit. physikal Chem.*, 1902, **41**, 601.

Urea Oxalate, $2CO(NH_2)_2,C_2O_4H_2$.—This salt separates out in the form of monoclinic tablets when a solution of urea is mixed with a concentrated solution of oxalic acid.

Urea not only unites with acids but also with a variety of salts and oxides. Thus, for instance, it forms with common salt the compound $CO(NH_2)_2 + NaCl + H_2O$. This substance crystallises from aqueous solution in large glittering rhombic prisms. Urea also forms similar compounds with certain other chlorides and nitrates.

When treated with a solution of caustic potash in the cold, it does not yield any ammonia, but on warming it is gradually resolved into ammonia and carbon dioxide, ammonium cyanate being probably the first product. Sodium hypobromite oxidises it to nitrogen, carbon dioxide and water, and it is also at once oxidised by nitrous acid or anhydride, with liberation of the nitrogen of both compounds in the free state and formation of water if the solution be warm :—

$$CO(NH_2)_2 + N_2O_3 = CO_2 + 2N_2 + 2H_2O.$$

In the cold ammonium carbonate is also formed :[1]—

$$2CO(NH_2)_2 + N_2O_3 = (NH_4)_2CO_3 + 2N_2 + CO_2.$$

Neutral potassium permanganate solution has no action on urea in the cold, and very little at 100°, but the acidified solution causes the rapid evolution of 1 volume of nitrogen and 2 volumes of carbon dioxide at 100°. Solutions of urea evaporated with silver nitrate yield ammonium nitrate and silver cyanate.

THIOCARBAMIC ACID, $CS\begin{cases}NH_2\\SH\end{cases}$.

487 The constitution of this compound, originally described under the name of hydrothiosulphoprussic acid,[2] was first pointed out by Debus.[3] The ammonium salt of this acid is formed by the union of carbon bisulphide with dry ammonia in presence of absolute alcohol; the salt separates out, after some time, in prismatic crystals. When hydrochloric acid is added to its aqueous solution, free thiocarbamic acid separates out. This substance is an oil at the ordinary temperature, but below 10° it forms a crystalline mass.[4] It has a smell resembling that of

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[1] Claus, *Ber.* 1871, **4**, 1440.

[2] Zeise, *Annalen*, 1843, **48**, 95.

[3] *Annalen*, 1850, **73**, 26.

[4] Mulder, *J. pr. Chem.* 1867, **101**, 401, and 1868, **103**, 178.

sulphuretted hydrogen, possesses an acid reaction, and is easily decomposed into sulphuretted hydrogen and thiocyanic acid, NCSH.

THIO-UREA, OR THIOCARBAMIDE, $CS(NH_2)_2$.

488 Reynolds[1] was the first to prepare this sulphur analogue of urea, which is formed by a reaction analogous to that by which common urea is obtained. A molecular change takes place in ammonium thiocyanate, $NCS(NH_4)$, when heated to 140°, corresponding to that observed in the case of ammonium cyanate. At the same time a quantity of guanidine thiocyanate is formed, while a portion of the thiocyanate remains unchanged.[2] In order to separate these three bodies, the melted mass is treated with two-thirds its weight of cold water, when the greater portion of the thio-urea remains behind. This is then dried on a porous plate, and purified by recrystallisation from hot water. According to Claus, it is not necessary to prepare ammonium thiocyanate for this purpose, but a solution of the crude salt obtained by dissolving carbon bisulphide in alcoholic ammonia may be employed; this is quickly evaporated, until ammonia, ammonium sulphide, and carbon bisulphide are abundantly evolved, and then the residue treated as above described. As long as thio-urea is not perfectly pure it crystallises in silky needles, but in the pure condition it forms magnificent large rhombic prisms or thick tables. It dissolves in eleven parts of cold water, and on heating with water to 140° is reconverted into ammonium thiocyanate. Heated by itself to 170—180° it is converted into guanidine thiocyanate and ammonium thiocarbonate. Like common urea, thio-urea forms compounds with acids, salts, and oxides. A characteristic compound is the *nitrate*, $CS(NH_2)_2,NO_3H$, which crystallises exceedingly well.

Seleno-urea, $CSe(NH_2)_2$, has also been prepared.[3]

PHOSPHORUS TRICYANIDE, $P(CN)_3$.

489 In order to prepare this compound a mixture of phosphorus trichloride and dry silver cyanide is heated in closed

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[1] *Journ. Chem. Soc.* 1855, 1.

[2] J. Volhard, *Ber.* 1874, **7**, 92, and *J. pr. Chem.* 1874, [2], **9**, 6; see also *Journ. Chem. Soc.*, 1903, 1; 1904, 403.

[3] Verneuil, *Compt. Rend.* 1884, **99**, 1154.

tubes for several hours to a temperature of 120–140°. When cold the tubes are opened, the excess of phosphorus trichloride driven off by moderate heating, and the residue brought into a tubulated retort, and heated in an oil-bath to 130–140° in a stream of carbon dioxide. The phosphorus tricyanide sublimes in long glistening white needles or thick plates. It takes fire when slightly warmed, and burns in the air with a bright white flame; it is decomposed by water into hydrocyanic and phosphorous acids;[1] thus:—

$$P(CN)_3 + 3H_2O = P(OH)_3 + 3HCN.$$

ARSENIC TRICYANIDE, $As(CN)_3$.

490 This substance is obtained by the action of finely divided arsenic on cyanogen iodide in presence of carbon bisulphide. It forms yellowish microscopic crystals, and is rapidly attacked by atmospheric moisture, and almost instantaneously by water, with formation of arsenious and hydrocyanic acids.[2]

BORON CARBIDE OR CARBON BORIDE, BC OR B_2C_2.

491 This is prepared by heating a mixture of boric anhydride and carbon in an electric furnace, and forms a graphite-like powder which melts at a very high temperature, burns with difficulty in oxygen, is insoluble in the usual solvents, but is decomposed by fusion with alkalis.[3]

Another boride of carbon, having the composition CB_6, is prepared by heating sixty-six parts of amorphous boron and twelve parts of carbon, obtained from sugar, in an electric furnace, or by dissolving the two elements in iron, copper, or silver at a very high temperature, and removing the metal by treatment with aqua regia. It forms very hard black lustrous crystals, having a density of 2·41, which are attacked by chlorine below 1,000°, and by oxygen very slowly at that temperature; like the previous compound, it is decomposed by fusion with alkalis. The powder is sufficiently hard to cut the diamond but more slowly than diamond dust.[4]

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[1] Wehrhane and Hübner, *Annalen*, 1863, **128**, 254, and 1864, **132**, 277.

[2] Guenez, *Compt. Rend.* 1892, **114**, 1186.

[3] Mühlhäuser, *Zeit. anorg. Chem.* 1893, **5**, 92.

[4] Moissan, *Compt. Rend.* 1894, **118**, 556.

THE GAS INDUSTRY.

492 The manufacture of gaseous fuel from coal and other carbonaceous matter, and its employment for the purposes of illumination, heating, and production of power, forms one of the largest of modern industries, and is a matter which has a most important bearing on almost all other manufacturing processes, inasmuch as there are few of these which are not greatly affected by cheapness of production of power, heat or light.

As early as 1726 it was noticed that an inflammable gas is evolved when coal is heated in a closed vessel, this observation having been published by Stephen Hales in that year, in his *Vegetable Staticks*, wherein he states that, by the distillation of 128 grains of Newcastle coal he obtained 180 cubic inches of an inflammable gas which weighed 51 grains. Bishop Watson, in his *Chemical Essays* (1761), describes experiments made on coal-gas, and mentions that it does not lose its illuminating power when it is passed through water. The first to apply these facts practically to the manufacture of coal-gas was William Murdoch, a Scotchman living at Redruth in Cornwall. He distilled coal in an iron retort, and lighted his house with the gas which he thus manufactured. Murdoch was afterwards employed in the celebrated engine works of Boulton and Watt at Soho near Birmingham. Whilst there he improved his process for the manufacture of gas, and in 1798 the Soho factory was for the first time lighted with coal-gas. In 1802 there was a public display of gas illumination at Soho in honour of the Peace ot Amiens; and during the next three years Murdoch's process became so far perfected that in 1805 the large cotton mill of Messrs. Phillips and Lee in Manchester was lighted with gas.

The success of this undertaking attracted the attention of several men of ability, especially Dr. William Henry and Mr. Clegg. To the former we owe the first accurate investigation of the chemical composition of coal-gas; to the latter we are indebted for many of the mechanical inventions still in use for its preparation and purification, without which the present enormous extension of the manufacture would have been impossible.

The streets ot London were not lighted with gas until 1812, and it was not introduced into Paris until after the peace of 1815.

Until the last quarter of the nineteenth century, the gas thus obtained was used almost exclusively for illuminating purposes, but during the past thirty years extensive developments have taken place in the use of such gas for purposes of heating, such as gas-fires and cooking stoves, and for employment in gas-engines for the production of power. Simultaneously great progress has been made in the production of gas having no illuminating power, but of sufficient calorific power for employment in gas-engines and for heating furnaces.

COAL-GAS.

493 When coal is subjected to dry distillation in closed retorts, a very complex series of changes takes place, the nature of which depends very largely on the temperature at which the distillation is carried out. When the temperature is only slightly above that at which decomposition commences, the volatile products formed consist chiefly of liquids of somewhat similar constitution to those contained in petroleum oil, the gases formed being small in volume and of high illuminating power. When the temperature is raised, the volatile products first produced undergo further changes in contact with the red-hot coke and with the surface of the retort through or over which they have to pass, and by the action of radiant heat whereby they yield on the one hand hydrogen and the simpler hydrocarbons such as methane, ethylene, &c., and on the other more complex substances belonging to the aromatic series, such as benzene, toluene, naphthalene, and anthracene. As the temperature is further raised, the quantity of hydrogen formed increases, with simultaneous production of more and more complex hydrocarbons containing smaller percentages of hydrogen, and if a sufficiently high temperature could be obtained, the sole products would in all probability consist simply of carbon and hydrogen.

Generally therefore, the higher the heat of distillation, the greater is the volume of the gas produced, and the lower its quality as an illuminating agent, whilst the condensable tar obtained decreases in quantity, but increases in specific gravity, owing to the presence of a larger proportion of heavy and high-boiling constituents.

In addition to carbon and hydrogen, coal always contains nitrogen, oxygen, and sulphur as well as mineral matter. The nitrogen is partly retained in the coke, and partly evolved as condensable products such as pyridine and quinoline, which are found in the tar, whilst about one-third is evolved in the form of ammonia. In addition free nitrogen and small quantities of hydrocyanic acid are evolved, the former being probably produced by the dissociation of the ammonia first evolved, and the latter by the action of free nitrogen on the red-hot coke.

The oxygen is chiefly found in combination either as steam, carbon monoxide, or dioxide; a small quantity is, however, converted into condensable products such as phenol, found in the tar. The sulphur partly remains in the coke, and partly forms sulphur compounds condensed with the tar, but a large proportion is evolved as sulphuretted hydrogen, mixed with smaller quantities of carbon bisulphide and other volatile sulphur compounds.

About 70 per cent. of the coal remains behind in the retort as coke, which consists chiefly of carbon, but always retains small quantities of nitrogen, oxygen, and sulphur as well as the whole of the ash present in the coal used. The coals employed for gas-making purposes are almost always caking coals, which on heating first become plastic, and then undergo carbonisation, so that the coke forms a more or less coherent mass, and does not retain the form ot the original coal. Non-caking coals usually contain less volatile matter and yield a coke possessing the form of the original coal, and commercially less valuable, so that these are unsuitable for the economical production of coal-gas, and are employed for steam-raising in boilers, and for the manufacture of producer-gas, &c. (p. 869).

The carbonisation of coal in the coal-gas manufacture is still almost invariably carried out in the same general manner as in Murdoch's day, namely, in long narrow retorts. Originally these were made of cast-iron, but fire-clay retorts were soon introduced, and are now always employed in all but the very smallest works. The section of these is oval or approximating in shape to the letter D, some of the shapes employed being shown in Figs. 194, 195, 196. The retorts are sometimes permanently closed at one end, and then vary from 8—10 feet in length, 14—22 inches in width, and 12—16 inches in depth, and contain a charge of 1·5—3 cwts. At present, in large works especially, retorts of double this length are employed capable of being opened at each end, and termed "through" retorts.

An iron mouthpiece, shown in section in Fig. 197, and in

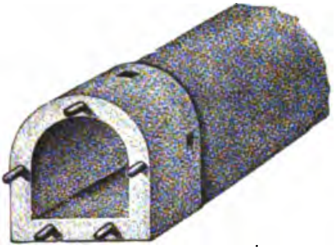

FIG. 194.

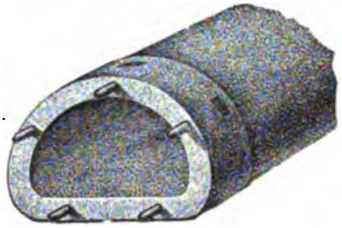

FIG. 195.

FIG. 196.

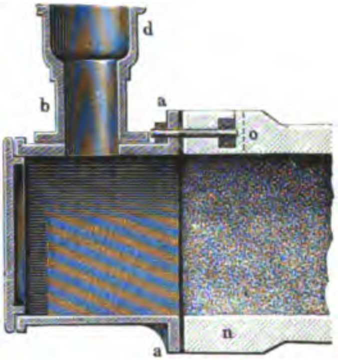

FIG. 197.

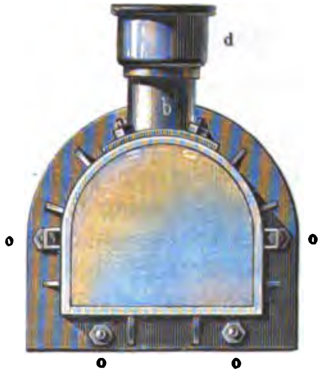

FIG. 198.

FIG. 199.

end elevation in Fig. 198, is attached to the open end or ends of the retort by means of bolts, and when the charge has been added, the end of the mouthpiece is closed by an iron lid,

Fig. 199, held in position by means of a holdfast and screw or other suitable arrangement.

A number of retorts, varying from 5 to 10 and sometimes 12, are usually arranged in a single setting and heated by means of a furnace, fed with a portion of the coke drawn from the retorts. In most modern settings, a deep furnace is used, placed below the level of the lowest retorts, and the latter are heated by "gaseous" firing, *i.e.*, by admitting below the bars of the furnace only such a quantity of "primary" air that the carbon of the fuel burns chiefly to carbon monoxide, which passes, together with the nitrogen of the added air, through the nostril holes of the furnace arch, and there meets with a current of "secondary" air, and burns in the setting around the retorts with formation of carbon dioxide, heating them uniformly (see p. 870). In many cases the secondary air is previously raised in temperature by means of the heat of the waste gases, which on their way to the chimney pass in zig-zag flues through a regenerator, the secondary air passing in the opposite direction through parallel flues, separated from the former by thin gas-tight walls. Figs. 200, 201, show the construction of a setting of seven retorts, Fig. 200, giving a tranverse section, and Fig. 201, a longitudinal section.

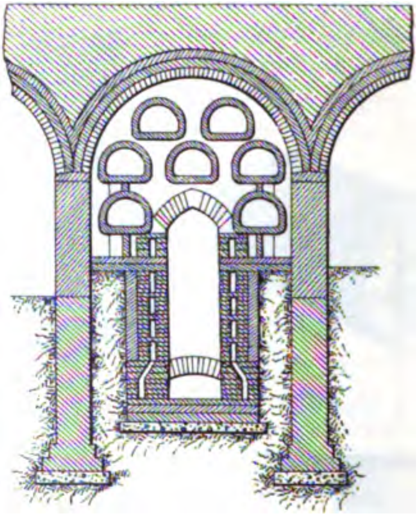

FIG. 200.

The charging of the coal and withdrawing of the coke is now frequently carried out by machinery instead of by hand, and in recent years the retorts have in many cases been set at an angle of about 32° instead of in a horizontal position, the coal being then charged by gravity from the upper end, and the coke, after carbonisation, discharged in a similar manner from the lower end.

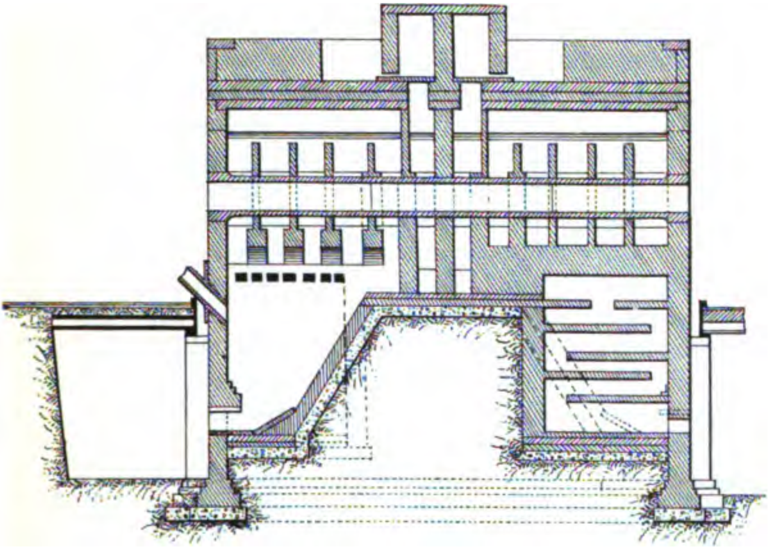

FIG. 201.

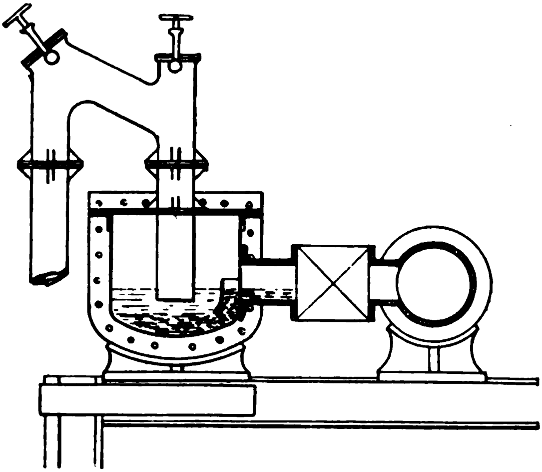

FIG. 202.

The retorts are usually heated to a temperature of from 1700—1850° F. (920—1000° C.), and a charge of 6—7 cwt. is then completely carbonised in 4—6 hours according to the nature of the coal.

The volatile products of carbonisation escape by means of the wide upright tube *d* (Figs. 197, 198), cast on to the mouthpiece, and pass thence through the ascension-pipe, bridge-pipe, and dip-pipe shown in Fig. 202, into the *hydraulic main.* This consists of a long horizontal trough, traversing the whole length of the retort bench, and serves as the collecting main for the volatile products from the whole of the retorts in the bench. In its passage through these pipes the gas undergoes rapid cooling, and deposits a large proportion of the tar and aqueous vapour, the separated water simultaneously absorbing ammonia, sulphuretted hydrogen and carbon dioxide from the crude gas, forming ammoniacal liquor. These liquid products are allowed to flow away continuously from the hydraulic main, but the overflows are arranged in such a manner that either tar or liquor (preferably the latter) is maintained at such a level that the dip-pipes are sealed in it to a constant depth, usually 1—2 inches. The gas can then readily escape from the retort by bubbling through the liquid, but when the retort lid is opened for charging or discharging, no gas can return from the hydraulic main through the ascension pipe, and burn at the mouth of the retort.

494 When the gaseous products leave the hydraulic main their temperature has been reduced to about 120—140° F., or 50—60° C., and they are then conveyed by mains known as the *foul-mains* to the condenser, where they are further cooled to a temperature approximating to that of the atmosphere, which results in the separation of a further quantity of tar and ammoniacal liquor. In this country the cooling is largely carried out by means of atmospheric condensers, and although many forms differing in external appearance are employed, the arrangement is in all cases such that the gas passes slowly through apparatus exposing a large surface to the atmosphere, whereby the sensible heat of the gases and latent heat of the condensed vapours is given up to the air passing over the surface. An example of a vertical pipe condenser is given in Figs. 203 and 204. Water condensers are also frequently employed either alone or subsequent to the atmospheric condensers; in these the gas passes through tubes surrounded by water, which is continuously

pumped through the apparatus in the opposite direction to the gas stream, so that the gas leaving the apparatus is finally cooled by the incoming cold water.

The object aimed at in condensation is not merely to cool the gas, but also to carry out the cooling in such a manner as to leave in it as much of the most volatile constituents of the tar (chiefly benzene and toluene) as it can retain at the lowest temperature to which it may subsequently be exposed during distribution, and at the same time to eliminate as completely as possible all vapours of higher boiling substances, especially naphthalene. The retention of benzene vapour is of importance, inasmuch as the illuminating power of the gas depends largely upon the amount of this vapour present, which also affects the calorific power, although to a much smaller extent.

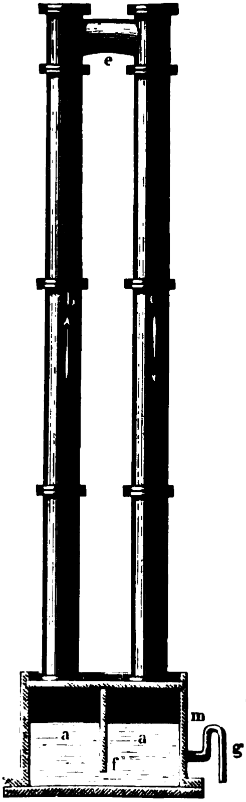

FIG. 203.

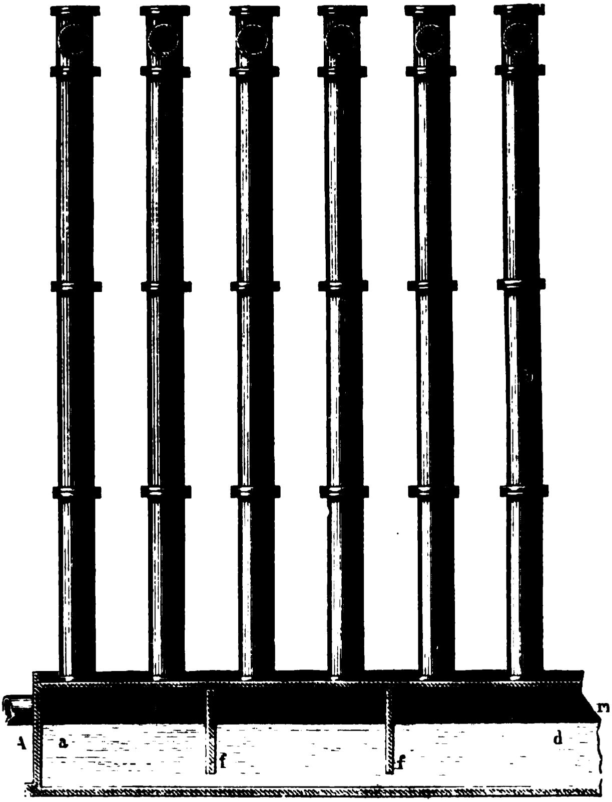

FIG. 204.

The removal of naphthalene is of vital importance, as otherwise the gas is liable to deposit solid naphthalene crystals in the subsequent manufacturing plant and distributing system, causing very serious inconvenience to both manufacturers and consumers.

The extent to which these objects are attained depends largely upon the manner in which the different products of condensation at various temperatures are brought in contact with the gas in its passage through the apparatus, but very little positive information is yet available as to the best system to adopt, and in consequence the greatest divergence occurs in practice. It is, however, generally agreed that the tar which separates at the earliest stage, viz., in the hydraulic main, should not be allowed to flow with the gas until the temperature of both is reduced to about that of the atmosphere, as otherwise this tar in cooling absorbs from the gas a quantity of benzene vapour, &c., which is retained by the gas if this portion of the tar is removed whilst still hot.

495 The gas after cooling usually passes to the exhausters, which pump the gas continuously as it is made, from the retorts through the condensers, maintaining a slight vacuum in this portion of the plant, and then force it forward under pressure through the subsequent purifying plant into the gas-holders. If no exhauster were used, the whole of the pressure required to force the gas through the apparatus and to lift the holders, equivalent to 15—40 inches of water, would be thrown on to the fire-clay retorts, and owing to their porous nature much loss of gas would ensue. Care must, however, always be taken that the vacuum maintained by the exhauster is not sufficiently great to cause air to be drawn into the hydraulic main through the dip-pipes when the retort lids are open.

The cooled gas as it leaves the condensers always contains a considerable quantity of suspended tarry particles, sometimes known as "tar-fog." To remove these a special apparatus is frequently employed wherein the gas is subdivided into fine streams, which then impinge on a solid surface to which the liquid tar particles adhere. In this country it is more usual to pass the gas in fine streams through a washer containing weak ammoniacal liquor derived from the condensers or other portions of the plant, by which means not only is the tar removed, but the weak liquor takes up a further quantity of ammonia from the gas as well as sulphuretted hydrogen and carbon dioxide. To effect the final removal of the ammonia the gas is passed through *scrubbers* in which it is treated with fresh water. For this purpose tall towers are largely employed, filled with coke, broken bricks, or thin boards on edge, thus exposing a large wetted surface to the gas, which passes upwards through the tower, and, finally, at the top comes in contact with the fresh water entering the apparatus and is thus completely freed from ammonia. Simultaneously, further quantities of sulphuretted hydrogen and carbon dioxide are removed by combining with the aqueous ammonia, forming ammonium sulphide and carbonate. In place of the tower scrubbers, mechanical rotary washers are now largely used, one form of which is shown in Fig. 205. This consists of a horizontal cylindrical shell, divided internally into compartments by vertical plates having an opening in the centre. A circular iron plate is placed in the middle of each compartment and keyed on to a central revolving shaft, and to each side of this plate are fixed circular brushes pressing on to both division plates forming the compartment. The gas in traversing the apparatus, as shown by the arrows, is compelled to pass through the brushes, which are kept constantly wetted by the liquor at the bottom of each compartment. The washing water enters at the gas-outlet end, and flows continuously through each compartment to the opposite end of the washer, and away from that end, by means of a syphon, to the liquor-well.

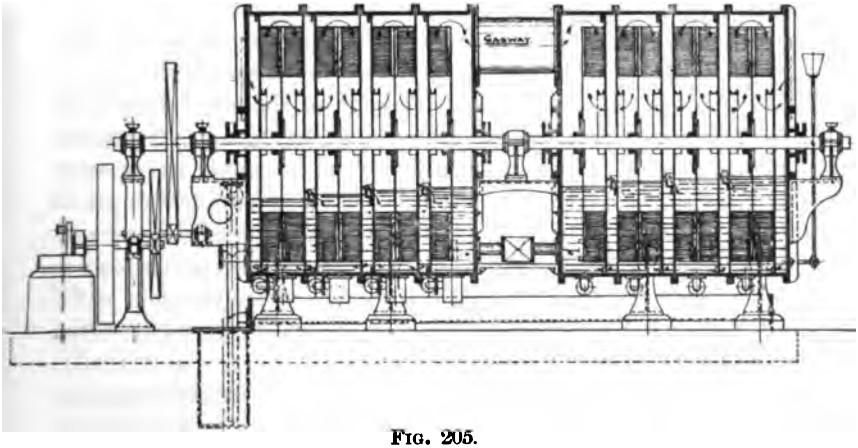

Fig. 205.

496 *Dry purification.*—After removal of the ammonia the

gas still contains the following impurities: Sulphuretted hydrogen, 1—2 per cent., or 600—1,200 grains per 100 cubic feet; carbonic acid, 1—3 per cent., or 800—2,400 grains per 100 cubic feet; carbon bisulphide, 15—50 grains per 100 cubic feet; in addition, the gas mostly contains 7—8 grains of sulphur per 100 cubic feet, in the form of thiophen and other organic sulphur compounds. The quantity of sulphur compounds present in the gas must be reduced to a low limit, inasmuch as they give rise to sulphur dioxide, and, finally, to sulphuric acid when burnt. All gas supplied for illuminating purposes must, in accordance with the Gas Works (Clauses) Act, be entirely freed from sulphuretted hydrogen, and in some cases a partial removal of the carbon bisulphide, present in much smaller quantity, is also required.

Carbonic acid is also an undesirable constituent of the gas, inasmuch as it depreciates the illuminating power to the extent of 3 to 3·5 per cent. for each 1 per cent. of the gas present. It likewise depreciates the calorific power, but to a much smaller extent, namely, in direct proportion to the quantity present. Whether it is advisable to remove the carbonic acid depends partly upon the relative proportions of the gas used, on the one hand, for illuminating in open-flame burners, and, on the other, for purposes in which the calorific power is the factor of chief importance, and also upon the cost of eliminating it, which varies greatly according to local circumstances.

The removal of these impurities is carried out by means of solid absorbents, which are placed in layers on wooden grids in large cast-iron boxes termed *purifiers*. The covers of these boxes are removable, to allow of the boxes being charged with fresh material or for the removal of the spent mass; these are made gas-tight by means of a rubber joint, or else are provided with vertical sides which dip into a lute of water surrounding the purifier, thus preventing any escape of gas so long as the depth of the water seal is greater than the pressure of the gas.

Where no attempt is made to remove sulphur compounds other than sulphuretted hydrogen, the gas is passed through a series of purifiers containing layers of hydrated oxide of iron, which absorbs the sulphuretted hydrogen, forming a mixture of ferrous and ferric sulphides:

$$Fe_2O_3.H_2O + 3H_2S = Fe_2S_3 + 4H_2O$$
$$Fe_2O_3.H_2O + 3H_2S = 2FeS + S + 4H_2O.$$

As soon as the gas passing into the last box is found to contain any quantity of sulphuretted hydrogen, the first box of the series is shut off, the "spent" oxide removed, and fresh oxide put in its place, the recharged box being then made the last of the series. The spent oxide is moistened and exposed to the air, and gradually undergoes oxidation, reforming ferric oxide and liberating sulphur.

$$2Fe_2S_3+3O_2+xH_2O=2Fe_2O_3+6S+xH_2O$$
$$4FeS+3O_2+xH_2O=2Fe_2O_3+4S+xH_2O.$$

The revivified material may then be again placed in the boxes for removal of a further quantity of sulphuretted hydrogen. The alternate process of conversion into sulphide and revivification is continued until the spent oxide contains 50—60 per cent. of sulphur, when it is sold for the manufacture of sulphuric acid. When the hydrocyanic acid of the crude gas has not been previously removed, the spent oxide frequently contains crude Prussian-blue, the amount of which is often sufficient to pay for extraction.

If a volume of oxygen equal to about half that of the sulphuretted hydrogen present be mixed with the crude gas before the purifiers, the above process of revivification takes place concurrently with the formation of sulphide, and the material lasts for a much longer period without changing, thus effecting a considerable economy in labour. The oxygen is always added in the form of air, the nitrogen of which causes a slight reduction in the illuminating power, necessitating the employment of a small additional quantity of better coal or oil to maintain the statutory illuminating power, but the saving in labour more than counterbalances this extra cost.

After the gas is freed from sulphuretted hydrogen the carbonic acid may be removed by the use of slaked lime in a similar set of purifiers, the latter being thereby converted into calcium carbonate. In this country a part at least of the carbonic acid is frequently removed in this way, but on the Continent the elimination is very rarely carried out.

When the purification is conducted in this manner, the carbon bisulphide present in the gas is but little affected. On the Continent almost universally, and in the majority of undertakings in this country, no further attempt is made to deal with this impurity. In certain towns, however, in addition to the requirement of entire freedom from sulphuretted hydrogen, a limit is placed on the amount of sulphur, in the form of carbon bisulphide or other sulphur compounds, which may be left in the gas; thus in London the limit in summer is 17 grains and in winter 22 grains per 100 cubic feet.

Only one absorbent has yet been found by which it is possible on a commercial scale to effect regularly even a partial removal of carbon bisulphide, namely, hydrated calcium sulphide. In order to carry out the more complete purification, the whole of the carbonic acid, and the greater portion of sulphuretted hydrogen, must be removed by means of lime, the latter giving rise to the formation of calcium hydrosulphide, which absorbs the carbon bisulphide. A common method is to pass the gas through a set of four boxes containing lime, the first two of which chiefly absorb carbon dioxide, the sulphuretted hydrogen being largely retained in the last two, giving rise to calcium hydrosulphide which effects the partial elimination of carbon bisulphide.

The nature of the reactions which take place in the absorption of the bisulphide is but little understood. It is probable that calcium thiocarbonate, $CaCS_3$, or some similar compound is formed, but nothing is known with certainty. It is found that the presence of oxygen in limited quantities is advantageous, but excess of the latter completely stops the absorption, inasmuch as the calcium sulphide is oxidised as fast as it is formed. If an excess of oxygen is accidentally admitted to purifiers which have previously been absorbing the bisulphide, the latter under the influence of the carbonic acid is again given off, and the gas may then contain far more bisulphide at the outlet than at the inlet of the purifiers. Frequently for no assignable cause, the absorption of bisulphide ceases, and does not again take place until the whole set of purifiers has been recharged with fresh lime. Moreover, the spent lime obtained has a most objectionable odour, and having practically no commercial value apart from a limited demand for agricultural purposes, it must be largely carted away at great expense; the smell caused by the material in the neighbourhood of the works and in the districts through which it is carted causes many complaints. This matter has recently (1904) been considered by a Board of Trade Committee, under the presidency of Lord Rayleigh, which has recommended that the obligation of the London Gas Companies to remove sulphur compounds other than sulphuretted hydrogen shall be abolished.

497 *Recovery of Cyanides.*—Owing to the greatly increased demand for cyanides in the gold-mining industry, many gas-undertakings now recover the hydrocyanic acid present in the crude gas. A number of different processes are in use for this purpose, the hydrocyanic acid being converted either into ferrocyanide or sulphocyanide. To obtain the former, the gas is treated in a washer with an iron salt in presence of an alkali, which results in the formation of the ferrocyanide of the alkali used. In some cases the ammonia present in the crude gas is utilised as the alkali, the gas being treated before the removal of the latter with a solution of ferrous sulphate, which is first converted into ferrous sulphide by the sulphuretted hydrogen also present, and then in conjunction with the ammonia and hydrocyanic acid yields a mixture of soluble ammonium ferrocyanide and insoluble double iron ammonium ferrocyanides. In other cases the gas is washed after removal of the ammonia with a mixture of ferrous sulphate or chloride with soda or lime, yielding a solution of sodium or calcium ferrocyanide, from which pure salts are obtained by subsequent treatment.

To recover the hydrocyanic acid as thiocyanate, the gas before removal of ammonia is passed through a washer containing ammoniacal liquor, to which sulphur is periodically added; the ammonium polysulphide first formed unites with the hydrocyanic acid, forming ammonium thiocyanate.

$$(NH_4)_2S_2 + HCN = NH_4CNS + (NH_4)HS.$$

A 30—40 per cent. solution of thiocyanate can be thus readily obtained, and is then sold to manufacturers for conversion into cyanide. The ammonium polysulphides also sometimes effect simultaneously a partial removal of carbon bisulphide.

After leaving the purifiers, the gas passes through the meters to the holders (the capacity of which is sometimes as much as 12,000,000 cubic feet), where it is stored and distributed as required.

One ton of coal yields from 9,000 to 12,000 cubic feet of gas according to the nature of the coal and the heat employed in its carbonisation, and there are simultaneously obtained from it 13—15 cwts. of coke, 8—11 gallons of tar, 20—35 gallons of "10 oz." ammoniacal liquor, *i.e.* liquor containing sufficient ammonia in 1 gallon to neutralise 1 oz. of pure sulphuric acid. The amount of cyanide produced generally varies from

1—5 lbs. of crystallised sodium ferrocyanide, $Na_4FeCy_6,10H_2O$ per ton.

498 *Composition of Coal-gas.*—Purified coal-gas obtained from common coal is a mixture of permanent gases and vapours, the relative proportions of the constituents varying according to the nature of the coal carbonised, and the heat employed in its distillation. The constituent present in the largest proportion is hydrogen, which usually forms about 50 per cent. of the whole, whilst from 32—35 per cent. consists of methane, and from 3—11 per cent. of carbon monoxide. These constituents burn with an almost non-luminous flame, the luminosity of the coal-gas flame being due to the presence of unsaturated hydrocarbon gases or vapours, the volume of which varies from 2—5 per cent. The great bulk of this hydrocarbon admixture consists of ethylene and benzene vapour, but smaller quantities of their higher homologues and of acetylene and naphthalene are usually present. In addition, nitrogen is always contained in the gas, together frequently with small quantities of oxygen and carbon dioxide, as well as of sulphur compounds which cannot be completely eliminated. The specific gravity of coal-gas varies from 0·42—0·5 (air = 1).

The following table gives the composition of samples of coal-gas from different sources.

COAL-GAS FROM BITUMINOUS COAL.

	London Gas. (Frankland.)		London. S. Metropolitan Gas. (Lewes.)
	a	*b*	
Hydrogen	50·05	51·24	57·08
Methane	32·87	35·28	33·99
Carbon monoxide	12·89	7·40	2·63
Unsaturated hydrocarbons	3·87	3·56	4·38
Nitrogen	—	2·24	0·15
Carbon dioxide	0·32	0·28	0·79
Oxygen	—	—	0·96
Carbon bisulphide	—	—	0·02
	100·00	100·00	100·00

Cannel Gas.—The gas obtained from cannel coal has a much higher illuminating power than that obtained from common coal, owing to the presence of a much greater percentage of methane and unsaturated hydrocarbons and a smaller percentage of hydrogen, as will be seen from the following analyses.

COAL-GAS FROM CANNEL COAL.

	Manchester Gas. (Bunsen & Roscoe.)	Manchester Gas. (C. R. A. Wright.)	Rochdale Gas. (C. R. A. Wright.)	London Cannel Gas. (Frankland.)
Hydrogen	45·58	52·71	53·44	35·94
Methane	34·90	31·05	29·87	41·99
Carbon monoxide . . .	6·64	4·47	5·86	10·07
Unsaturated hydrocarbons.	6·46	11·19	10·83	10·81
Nitrogen	2·46	—	—	—
Carbon dioxide	3·67	0·58	—	1·19
Oxygen	—	—	—	—
Sulphuretted hydrogen . .	0·29	—	—	—
	100·00	100·00	100·00	100·00

Owing to the increasing scarcity and consequently high price of cannel, the amount of such gas produced is steadily diminishing, and is now confined to the neighbourhood of the cannel fields, such as parts of Lancashire and Scotland. A small percentage of cannel coal was also formerly almost always carbonised with common coal in order to increase somewhat the illuminating power of the resulting gas, but the present tendency is either to reduce the statutory quality of the gas to that given by the common coal without admixture of cannel, or else to raise the illuminating power by an admixture of carburetted water gas.

It has already been pointed out that the effect of increased temperatures of carbonisation is to increase the percentage of hydrogen, and to decrease that of methane and unsaturated hydrocarbons. When the coal is first charged into the retort, the temperature of the latter is reduced by the cold mass, so that a much richer gas is produced in the early stage of distillation. Moreover, as the carbonisation proceeds, the gas coming off from the interior of the charge has to percolate through the surrounding red-hot mass of coke, which tends to convert the gaseous hydrocarbons into denser compounds and hydrogen.

The following table shows the composition of the gas evolved from a Derbyshire gas-coal at different periods after charging.

The samples were aspirated from the ascension pipe and drawn through dilute sulphuric acid to remove tarry matters and ammonia. The temperature of the retort was about 950° C.

Hours after commencement	½ hour.	1½ hours.	2½ hours.	3½ hours.	5 hours.
Sulphuretted hydrogen .	3·8	3·1	2·8	2·1	1·2
Carbon dioxide	3·0	2·8	2·6	2·3	1·7
Unsaturated hydrocarbons	8·65	5·2	3·6	2·4	0·0
Oxygen	0·0	0·0	0·0	0·0	trace
Carbon monoxide . . .	4·35	5·0	4·9	4·5	3·8
Hydrogen	29·8	37·5	42·2	46·2	60·8
Saturated hydrocarbons .	49·7	42·05	39·4	37·5	26·3
Nitrogen (by difference) .	0·7	4·35	4·5	5·0	6·2

The percentage of saturated and unsaturated hydrocarbons, sulphuretted hydrogen, and carbon dioxide steadily decreases, whilst that of hydrogen increases, and that of carbon monoxide remains nearly constant. The maximum production of carbon bisulphide is at about the middle of the period and hydrocyanic acid appears to be chiefly formed towards the end.

499 *Illuminating Power and Calorific Power of Coal-gas.*—The comparative value of coal-gas to a consumer mainly depends upon its illuminating and calorific power. Formerly, when the gas was almost exclusively used for illuminating with open flame burners, only the former value was of importance, but at the present time, when so large a proportion of the gas is used for incandescent burners, gas fires, and gas engines, the calorific power is often of greater importance than the illuminating power.

It is impossible to assign to any gas a definite illuminating power, as this is not an absolute property of the gas, but varies with the same sample according to the kind of burner used, the rate at which it is burnt, and to a smaller extent with the atmospheric moisture and barometric pressure. All that can be done, therefore, is to burn the gas under conditions which are made as nearly uniform as possible, and to determine the comparative illuminating power under these conditions.

A definite standard of light is also essential, and in this country the legal standard is the quantity of light emitted by a sperm candle of specified composition and construction, burning at the rate of 120 grains per hour. Such candles have been found most unsatisfactory; it is impossible to construct them so as to burn at the above constant rate, and the rate of burning must therefore be always experimentally determined, and a correction made accordingly. Even with this correction, however, the amount of light is far from constant, and at the present time the candles are being largely replaced by the 10-candle Pentane Lamp devised by Vernon Harcourt. In this standard, a regulated current of air saturated with pentane vapour is burned in a specially constructed Argand burner, so as to give a constant height of flame, the upper portion of which is screened off to such an extent that the unscreened portion gives a light equal to 10 standard candles. The lamp is very much more constant than candles, but is still liable to a variation of about 5 per cent. under the varying conditions of temperature, pressure and moisture content of the atmosphere.

The standard burner mostly employed is the London Argand, originally constructed in 1868, for gas of the quality then made in London, the air supply to the centre of the flame and around it within the chimney being such as was most suitable for burning gas of that general composition when the rate of consumption was 5 cubic feet per hour.

In making the comparison between the standard light and that of the gas, advantage is taken of the physical law that the intensity of the illumination from a luminous point is inversely proportional to the square of the distance of the illuminated surface from that point. All that is necessary is to ascertain the distances at which the candle and standard gas flame both produce the same illuminating effect, the illuminating power being then calculated from these observations. In Bunsen's bar photometer the candles and gas flame are fixed at the end of a graduated bar, usually sixty inches in length, and the illuminated surface consists of a diaphragm of paper, Fig. 206, which, with the exception of a small circle in the centre, has been painted with a solution of spermaceti in benzene, thus rendering the disc, with the exception of the central portion, transparent. If, therefore, the disc is more strongly illuminated on one side than the other, a difference is observed between the

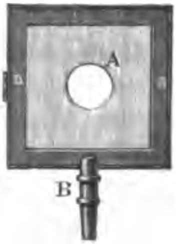

FIG. 206.

two portions of the disc, but when both sides are equally illuminated this difference disappears. The disc is fixed at right angles to the bar in a carriage which can be moved in either direction along the bar, and at the back of the box containing the disc are placed two inclined mirrors which enable the observer looking at the diaphragm in a direction at right angles to the bar to see simultaneously a reflection of both sides of the disc. The disc carriage is then moved along the bar until the point is found at which the whole surface of the disc on both sides appears equally illuminated. If the distance of the standard from the point thus found is a, and that of the gas burner b, the relative value of the two lights is $\frac{a^2}{b^2}$, and from the known value of the standard, and the rate of consumption of gas in the burner, measured by an experimental meter, the illuminating power can be readily calculated, the figures being always given for a rate of consumption of 5 cubic feet per hour.

In Harcourt's table photometer, the standard of light and the gas burner are placed in fixed positions in such a manner that each illuminates two adjacent portions of a translucent piece of white paper placed in a fixed "photoped," and the gas consumption is varied until the illumination of the two portions is exactly equal. The standard and gas burner are fixed at distances of 1 meter and 1·269 meters respectively from the photoped, so that, when equality of light is obtained, the amount of light given by the gas is $\frac{(1{\cdot}269)^2}{(1{\cdot}000)^2} = 1{\cdot}6$, and as the value of the Harcourt standard is 10 candles, that of the gas must be 16 candles. From the observed rate of consumption the value for 5 cubic feet per hour can be readily determined.

As the volume of the gas varies with the temperature and barometric pressure, these must always be taken, and the gas consumption reduced to a standard temperature and pressure, which in this country is 60° F. and 30 inches of mercury.

500 *Calorific Power of Gas.*—Unlike the illuminating power, the calorific power of any combustible gas is an absolute property, and in reality gives the total potential energy of chemical combination, expressed in heat units. Provided the combustion of the gas is complete, the calorific power of the same gas remains constant whatever the type of burner or rate of combustion. In this country the calorific power is expressed in terms of British

Thermal Units per cubic foot, the B.Th.U., being the amount of heat required to raise 1lb. of water 1° F.

In determining the calorific power, the gas is burnt in the chamber of a suitable calorimeter, and the products of combustion pass through a series of tubes or annular chambers, around which water is flowing in the opposite direction to the current of the waste gas. The latter thereby gives up its heat to the water, thus increasing the temperature of the latter by an amount readily determined by observation of thermometers placed on the inlet and outlet of the water stream. As soon as this value is found to remain nearly constant, a reading of the gas meter is taken, and the water collected, frequent observations of the water thermometers being made. As soon as the measuring vessel is filled, the gas is shut off, the quantity burnt noted (generally from 0·1 to 1 cubic foot), and the average difference in the temperature of the ingoing and outflowing water calculated from the readings taken. The calorific power is then found from the equation

$$\text{Cal. power} = \frac{\text{lbs. of water collected} \times \text{difference in temp. (F}^\circ\text{).,}}{\text{volume of gas passed}}$$

the usual correction being also made for effect of temperature and barometric pressure on the volume of gas burnt.

The calorific power thus obtained is the "gross" value, that is, the number of heat units evolved when the steam formed in the combustion is condensed to water, and therefore includes the latent heat of such steam. In actual practice, however, the steam usually passes away without condensation, so that this latent heat is rarely utilised. In making a calorific power test, therefore, the water condensed during the actual period of testing is collected and measured, and the amount of latent heat evolved in the condensation of this volume of water calculated and deducted from the above "gross" value. The figure thus obtained gives the "nett" calorific power, or the heating value when all the steam formed remains in the gaseous state.

The gross calorific power of 16 candle coal-gas generally varies from 600—650 B.Th.U., the nett value being about 10 per cent. less. There is, however, no constant relation between the illuminating and calorific powers, owing to the fact that variations in the composition of the gas affect them in different ways. Thus, for example, the addition of methane to a sample of coal-gas decreases its illuminating power, but increases the heating power, pure methane having a calorific power of 1024 B.Th.U.

On the average it is found that the calorific power of gas increases with increasing illuminating power, but the proportional increase is much smaller in the former value. Conversely, the calorific power decreases much more slowly than the illuminating power, and coal-gas which has been deprived of all illuminating power by removal of unsaturated hydrocarbon vapours still has a calorific power of about 500 B.Th.U. gross.

In Germany, where the use of the incandescent burner is now almost universal, and open flames are hardly employed, no notice whatever is in many towns taken of the illuminating power, only the calorific power being determined, and it is probable that in the course of a few years a similar change will take place in this country.

The Welsbach incandescent burner depends largely for its luminosity on the temperature to which the mantle is raised, *i.e.* on the temperature of the flame. This depends not only on the calorific power of the gas, but also on the quantity of air required for its combustion, as well as on the construction of the burner and the pressure at which the gas is supplied. The lower qualities of gas require less oxygen for combustion than the richer gases, so that a smaller quantity of inert nitrogen is present in the flame to lower its temperature, and hence a gas of lower calorific value may give a higher flame temperature than that obtained with a richer gas.[1]

COKE OVENS.

501 The coke produced in gas works is too soft for many purposes, and hard coke is therefore largely manufactured, especially for use in metallurgical work. For this purpose the coal is carbonised in large chambers, instead of in the comparatively small retorts employed in gas manufacture. The gas evolved is employed for heating the ovens, and formerly all the tar and ammonia produced were wasted, but systems are now largely adopted, such as the Simon-Carvès, Semet-Solvay and Hofmann ovens, in which these by-products are recovered. In addition,

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[1] For further information see *Treatise on the Manufacture and Distribution of Coal-Gas* (Walter King, 11 Bolt Court, E.C.); Groves and Thorp's *Chemical Technology*, Vol. IV. *Gas Lighting*, C. Hunt (J. and A. Churchill); *Handbook for Gas Engineers and Managers*, W. Newbigging (Walter King); *Chemistry of Gas Manufacture*, W. J. A. Butterfield (Griffin).

the gas, after removal of tar and ammonia, is also frequently washed with tar-oil to recover the benzene vapour which it always contains. Owing to the great surface of heated coke over which the gas has to travel in the large ovens, its illuminating power is low, but it has a proportionally high calorific power. More gas is mostly produced than is actually required for heating the ovens, and this surplus is sometimes enriched with benzene vapour and used for illuminating purposes.

WOOD-GAS.

502 In countries where wood is cheap and coal dear, wood has been employed for the production of illuminating gas. The first to propose the use of this material was the French engineer Le Bon, at the end of the 18th century, and he is regarded in France as the originator of the Gas Industry. The gas obtained was of very low illuminating power, but in 1849 Pettenkofer, and later on Rüdinger, showed that if the gases first evolved are submitted to a high temperature, a better result is obtained, owing to the formation of dense hydrocarbons, and it was for some time manufactured in certain towns in Germany and Switzerland.

The following numbers give the average composition of wood-gas after removal of carbonic acid :—

	Per cent.
Heavy hydrocarbons (ethylene and its homologues)	10·6 to 6·5
Light „ (methane „ „)	35·3 to 9·4
Hydrogen	41·7 to 18·7
Carbon monoxide	61·8 to 22·3

Wood-tar consists of a mixture of a variety of substances, amongst which creosote is the most important. The watery distillate does not contain much ammonia in solution, but a number of organic products, such as acetone, wood-spirit (methyl alcohol), and acetic acid are present and are recovered on the large scale.

Very little if any wood-gas is now made for use as an illuminant, but the process is still carried out for the preparation of charcoal and the liquid products of the distillation.

OIL-GAS.

503 The preparation of illuminating gas by the dry distillation of oil was first carried out about the year 1815, the gas

being compressed in strong reservoirs, so as to allow of its being moved from place to place, being therefore known as "portable gas." The compressed gas always deposited a considerable quantity of liquid hydrocarbons, which were investigated about the year 1820 by Faraday, who was thus led to the discovery of benzene. The manufacture of oil-gas, however, was soon discontinued as it was unable to compete with the cheaper coal-gas. Since about the year 1870 the manufacture has been revived, owing chiefly to the demand for gas of high illuminating power for railway trains, where a small volume of the gas is required to last for a long period. It is also used to a considerable extent for lighthouses.

The oil employed is either a shale oil or a mineral oil having a specific gravity of 0·82—0·88, and its distillation is usually carried out by one of two processes, known as the Pintsch and Pope processes respectively. In the former two cast-iron retorts one above the other are employed, both being maintained at a bright cherry-red heat; the oil is allowed to drop at the rate of twelve gallons per hour on to a plate in the upper retort, where the non-volatile impurities remain, whilst the volatile portions pass through the lower retort where they are further carbonised. The purification of the gas is carried out in the same manner as with coal-gas, but is of a simpler nature inasmuch as the amount of sulphur compounds in the gas is small. Details of the Pope process have not been published; it is stated that the oil drops first into the lower retort, and the vapours then pass through the upper retort, but in other respects the two processes are probably similar. For lighting trains, etc., the gas is stored in reservoirs beneath the carriages under a pressure of about five atmospheres. The tar obtained from oil contains a comparatively small amount of benzene; it is therefore of little or no commercial value, and is usually employed for heating the retorts.[1]

Owing to the rise in the price of cannel coal, oil-gas has sometimes been used in its place for enriching coal-gas. In what is known as the "Peebles" process the retorts are heated only to a low redness, and the oil added in a fairly large stream; the gas evolved contains large quantities of undecomposed oil vapours, which separate in the liquid state in the condensers and after mixing with a certain proportion of fresh oil again

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[1] Ayres, *Proc. Inst. Civil Eng.* **93**, 298; see also Thorpe's *Dict.* vol. ii. p. 213.

pass back into the retort.[1] In this manner the formation of any liquid residuals is avoided, the sole products being a permanent gas of very high illuminating power and a dense black coke which remains behind in the retort. The gas is then mixed with the coal-gas in the proportion requisite to bring the latter up to the standard illuminating power.

WATER-GAS AND CARBURETTED WATER-GAS.

504 The theory of the production of water-gas has already been considered (p. 792). The manufacture of this gas has now attained very large proportions, especially in the United States. Water-gas burns with a non-luminous flame of very high temperature, and is sometimes employed for metallurgical purposes. The great bulk of the gas produced is at once mixed with either benzene vapour or oil-gas, the mixture being then known as "carburetted" water-gas, and for distinction the uncarburetted gas is frequently termed "blue" water-gas.

In the United States carburetted water-gas forms about 80 per cent. of the total gas production, and in this country it has also been largely manufactured during the past 10—15 years and mixed with coal-gas before distribution.

In the manufacture of "blue" water-gas, air is blown into a generator charged with anthracite or coke until the latter has attained a high temperature. The oxygen of the air combines with the carbon forming a mixture of carbon monoxide and dioxide, which passes out from the generator mixed with the nitrogen of the air, the carbon monoxide thus formed not being utilised as a rule, and thus causing loss of fuel. In the Dellwik-Fleischer apparatus, however, this loss is reduced to a small amount by using a higher pressure of air blast and smaller depth of fuel, whereby the carbon is almost entirely burnt to the dioxide. As soon as the fuel is sufficiently hot, the air blast is shut off and steam admitted, when water-gas is formed. The admission of steam is continued until the temperature of the fuel is reduced to such an extent that the percentage of carbon dioxide rises rapidly, and the steam is then shut off and the air blast again substituted. This cycle of operations is then continued with the necessary intervals for charging the generator with fresh fuel and removing the non-volatile products.

It will be seen that the process is an intermittent one, and

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[1] *Journ. Gas Lighting*, 1894, i. 1050.

various forms of apparatus have been devised in which the fuel is heated by an external furnace, but hitherto it has been found that the first is the cheaper and more reliable plan.

The composition of "blue" water-gas is seen from the following analysis:

Hydrogen	51·9
Carbon monoxide	39·6
Carbon dioxide	4·2
Nitrogen (by diff.)	2·9
Methane	0·8
Sulphuretted hydrogen	0·6
	100·0

It has a calorific power of about 300 B.Th.U. or about one-half that of London coal-gas, but as it only requires about 2·5 vols. of air for its complete combustion it gives a flame having a very high temperature.

In the manufacture of carburetted water-gas, in addition to the generator an apparatus is required wherein to gasify the oil used, and to heat the vapours thus formed so as to split them up into permanent gases, which then mix with the water-gas simultaneously passing through the apparatus. This is done in tall cylindrical vessels known as the "carburetter" and "superheater," which are filled with firebrick chequer work. The generator is worked in the same manner as in the production of "blue" water-gas, and the producer gas formed, which in this case must contain carbon monoxide, passes into the carburetter and superheater, where it meets a secondary supply of air and undergoes combustion within the apparatus, thus bringing the firebrick chequer work to a high temperature. The waste gases pass out into the atmosphere through a valve at the top of the superheater, known as the "stack-valve." When generator and brickwork are sufficiently hot all air is shut off, the stack-valve closed, and steam admitted into the generator, the water-gas formed passing through the carburetter and superheater, into the former of which oil is simultaneously pumped; the oil vapours mix with the hot water-gas, and in passing through the superheater are split up into permanent gases and condensable tarry matter. As soon as the temperature in the generator falls too low, the admission of oil is stopped, the steam replaced by air, and the whole raised to a high temperature as before.

By suitably regulating the quantity of oil admitted, gas of any illuminating power up to 30 candles can be obtained. The oil used is mostly that fraction of petroleum intermediate between the ordinary burning paraffin oil and the lubricating oils, and consists almost entirely of hydrocarbons. The condensation and purification of the gas is carried out in the same manner as with coal-gas, and the only bye-product formed in the process is oil-tar, amounting in quantity to about one-eighth of the oil used. This consists for the most part of aromatic hydrocarbons, and only contains small quantities of oxygen, nitrogen, and sulphur compounds, as the original oil contains but little of those elements.

The composition of purified carburetted water-gas is shown from the following typical analysis:

Hydrogen	39·44
Carbon monoxide	29·03
Saturated hydrocarbons .	16·88
Unsaturated hydrocarbons .	8·23
Nitrogen (by diff.) . . .	6·21
Oxygen	0·21
	100·00

The calorific power of this gas is about 10 per cent. lower than that of coal-gas having the same illuminating power.

ACETYLENE.

505 Acetylene is now manufactured on a large scale for use as an illuminant in places where coal-gas is not available, such as small villages and country houses or railway stations. The method invariably adopted for its production is the action of water on calcium carbide. The latter substance was, as already mentioned, first prepared by Wöhler in 1862, who likewise observed the formation of acetylene from it by the action of water. The carbide was, however, first obtained in quantity in 1892 by a Canadian engineer named Willson, in an attempt to manufacture metallic calcium by heating lime with carbonaceous matter in the electric furnace, the resulting product being, however, calcium carbide. This was also independently obtained in the same manner at a slightly later date by Moissan.[1]

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[1] *Compt. Rend.* 1892, **115**, 1031.

The manufacture of acetylene from carbide was commenced about 1895, and since that date some hundreds of different forms of apparatus have been patented for carrying out the decomposition of the carbide with water. These may all be divided into two general classes: (1) those in which the water is added to the carbide, and (2) those in which the carbide is added to the water so that the latter is always in excess. The objection to generators of the first class is the higher temperature attained in the reaction, which results in the partial conversion of acetylene into tarry matters. Some generators of each class are constructed so as to render them "automatic," *i.e.* the generation of acetylene only takes place as fast as it is consumed, whilst in others the whole charge is decomposed at once, and the resulting gas stored in a holder for use as required.

In addition to acetylene, the gas obtained always contains appreciable quantities of phosphine, sulphuretted hydrogen and other sulphur compounds, and ammonia, derived from the calcium phosphide and sulphide and magnesium nitride which are almost always present in commercial calcium carbide, and these must be removed before the gas is burnt in rooms, the phosphine being especially obnoxious as it burns to phosphorus pentoxide, which forms a haze of phosphoric acid in the room where such impure gas is burnt. With generators of the second class the sulphuretted hydrogen and ammonia are largely retained by the water, but this has but little effect on the other sulphur compounds and the phosphine. For the complete purification three different agents are now in common use: (1) Bleaching powder, (2) an acid solution of copper and iron salts, (3) an acid solution of chromic acid. The two latter are frequently for convenience absorbed in kieselguhr, yielding a solid porous material, and are then sold under the names "frankoline" and "heratol," whilst the purifying substances termed "acagine" and "puratylene" consist of bleaching powder mixed with other material to form a suitable porous mass, the former containing in addition lead chromate.

Owing to the explosive nature of compressed acetylene (p. 770), the storage of gas under pressures exceeding that of the atmosphere by 100 inches of water is prohibited in this and many other countries. It may, however, be safely compressed in cylinders filled with porous material soaked in acetone, in which the gas is exceedingly soluble. The compression may also be safely carried out when the acetylene is mixed with about twice its volume of other combustible gas, such as coal-gas or oil-gas, and a mixture of the latter with acetylene has been employed in Germany for lighting railway carriages.

In order to develop the full illuminating power of the gas, and to prevent the smoking which so readily occurs with gas of high quality, it must be burned in special burners, and not in those usually employed for coal-gas. With a proper burner the light given off is equal to 240 candles, calculated at the rate of 5 cubic feet per hour, as compared with 14—18 candles in the case of coal-gas.[1]

MANUFACTURE OF FUEL GAS.

506 During the latter half of the last century many attempts were made to convert the whole of the combustible matter of coal and other carbonaceous matter into gas in a single operation, and to obtain in this manner a cheap gas which, although not of high calorific power, would have sufficient thermal value to be used in the heating of furnaces and steam boilers, and especially for direct employment in the production of power in internal combustion engines. Great advances have been recently made in this direction, and gaseous fuel of this type, generally known as *producer-gas*, is now employed to a very large extent.

The simplest method of obtaining such gaseous fuel, chiefly worked out by Siemens, is by admitting into the furnace containing the fuel only such a quantity of air that the carbon burns to carbon monoxide, the mixture of this gas with the nitrogen of the admitted air being then conveyed to the point where the heat is required, meeting there a secondary supply of air, which effects the complete combustion of the gas.

If it were possible to effect the production of carbon monoxide only, the resulting gas would consist of about 33 per cent. of that gas and 67 per cent. of nitrogen, but some carbon dioxide is always produced, 4 per cent. of the latter representing good working. Moreover, in order to prevent the furnace bars from

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[1] For further information with regard to the manufacture and use of acetylene, the following works may be consulted: *Acetylene*, by V. B. Lewes, 1900 (Constable); *Acetylene, its Manufacture and Uses*, by Leeds and Butterfield, 1903 (Griffin); *Handbuch für Acetylen*, Caro, Ludwig and Vogel, 1904 (Vieweg).

burning, water is continually kept running on to these, and drips into the ash-pan, which is kept full of water, so that a certain amount of steam is constantly evolved, and mixes with the air entering the generator, and in passing through the hot fuel is converted into water-gas. As the water-gas reaction takes place with absorption of heat, the fuel temperature is thereby kept lower, reducing the wear and tear of the fire-brick lining, and preventing the fusing of the clinker formed from the ash of the fuel, and making it more readily removable. The mixed gas therefore, in addition to carbon monoxide, carbon dioxide, and nitrogen, always contains hydrogen, and also a little methane derived from the hydrogen present in the fuel.

This method is employed in many forms of metallurgical furnaces, and is also used in most modern gas-works as the means of heating the retorts (p. 846), each bed being usually provided with its own generator. In some cases, however, generators are provided sufficiently large to heat several beds. Frequently the heat of the waste gases is employed to raise the temperature of the producer-gas, or of the secondary air, or of both before they meet, in order to effect further economy in fuel. The gas thus obtained has a calorific power of about 130 B.Th.U., and the general composition of the gas is shown on p. 872.

Of a rather different composition is the gas manufactured by the Dowson and other plants, which may be regarded as a mixture of producer-gas and water-gas. It has already been pointed out that the formation of water-gas takes place with absorption of heat, whereas the formation of carbon monoxide from carbon gives rise to evolution of heat, and it is therefore possible, by passing into the generator a mixture of steam and air in right proportion, to keep the mass of fuel at a fairly constant temperature, and thus to make the process continuous except for the necessary intervals for charging fresh fuel or removing the ashes. The resulting gas contains all the nitrogen of the added air, but has still a calorific power of 150–160 B.Th.U. Owing to the greater proportion of the steam employed, the percentage of hydrogen is much higher and that of nitrogen lower than with Siemens producer-gas, as will be seen from the analysis on p. 872.

The steam is supplied under pressure from a small boiler, and a gasholder is provided sufficiently large to store the gas required during the periods of charging and clinkering.

Recently, however, *suction gas-producers* have been brought into use in which air and steam under atmospheric pressure are drawn into the generator by the suction stroke of the gas engine which is being supplied; in these plants no separate steam-boiler or storage-holder is required, the gas being made as required by the action of the engine itself, when this has once been started.

"MOND" GAS.

507 In the case of the Dowson and similar plants, anthracite or coke is mostly used as the fuel in the generator, as the tar formed from bituminous fuel gives rise to great trouble in working. Under the patents of Mond and Duff, however, in which this difficulty has been to a considerable extent overcome, bituminous fuel is now being used for the production of fuel-gas on a very extensive scale. By the use of a large excess of steam, the temperature in the generator is kept so low, that practically the whole of the nitrogen of the coal is obtained as ammonia, whereas in the coal-gas manufacture only about one-third of the nitrogen is thus recovered.

In this process common bituminous slack is first fed into a bell at the top of the generator, where it undergoes a preliminary distillation, the volatile products passing downwards through the hot fuel before joining the bulk of gas leaving the producer. In this manner the tar is largely converted into permanent gas, and the partly carbonised slack then passes into the body of the producer, where it is acted on by an air blast saturated with steam at 85° C., and superheated by passing through the annular space around the producer. The quantity of steam admitted is 2·5 tons for every ton of fuel gasified, which prevents the formation of clinker and the destruction of ammonia, but enables the fuel to be thoroughly burned. The bottom of the generator is conical and is sealed in a tank of water, into which the ashes fall and are periodically removed without interrupting the gas making.

The hot gas and undecomposed steam leaving the generator first pass through a tubular regenerator, through which the incoming blast is passing in the opposite direction, this being thereby heated whilst the gas is partly cooled. The latter then passes through a washer, where it meets with a water spray thrown up by revolving dashers, and is thus cooled to about

90° C., and afterwards traverses a lead-lined tower filled with tiles over which a stream of acid liquor, containing ammonium sulphate with 2–4 per cent. of free sulphuric acid, is continuously pumped, the ammonia being thereby absorbed; to render the process continuous some of the liquor is constantly withdrawn from circulation, and a corresponding quantity of sulphuric acid added to the stream on its way to the tower. The gas, freed from ammonia, then passes to a further cooling tower, where it meets a downward flow of cold water, the gas being cooled and the steam condensed; the cooling water is at the same time heated, and passes to a third tower, where the blast on its way to the generator meets it, and is thereby raised to the temperature of about 73° C., and simultaneously saturated with steam at that temperature. By thus utilising the heat of the gases from the producer, nearly one ton of steam is added to the blast for each ton of fuel gasified.

The gas after cooling may be at once used for firing boilers or furnaces, but if required for gas engines, must be filtered to remove suspended dust and tarry particles.

Owing to the great excess of steam used in the generator, the reaction,

$$C+2H_2O=CO_2+2H_2,$$

takes place to a large extent, so that the resulting gas contains a much higher percentage of carbon dioxide and hydrogen and a lower percentage of carbon monoxide than Dowson gas, as will be seen from the analysis given below, but the average calorific power is about the same, namely, 150–160 B.Th.U. From one ton of slack a yield of 140,000 to 160,000 cubic feet of gas is obtained, according to the quality of the coal used.

Analyses of Producer-gas.

	Siemens Gas.	Dowson Gas.	Mond Gas.
Carbon dioxide . .	5·2	6·1	15·0
Carbon monoxide .	24·4	26·0	12·0
Hydrogen	8·6	18·5	28·0
Methane	2·4	0·3	2·0
Nitrogen	59·4	49·1	43·0
	100·0	100·0	100·0

SILICON OR SILICIUM. Si = 28·2. (H = 1.)
28·4. (O = 16.)

508 This element is, next to oxygen, the chief constituent of the earth's solid crust. It always occurs combined with oxygen in the form of silicon dioxide, or silica, SiO_2, known in the crystalline condition as tridymite, quartz, and the various kinds of sand and sandstone, and in the amorphous condition as opal, flint, &c. This substance combined with bases forms a large and important class of minerals termed the silicates, which occur very largely in many geological formations. For instance, granite and the allied primitive rocks contain between 20 and 36 per cent. of silicon.

Minerals rich in silica were used in ancient times by reason of their hardness as well as for the purpose of glass-making, and Becher believed that they contained a peculiar kind of earth, which he termed *terra vitrescibilis.* In the seventeenth century it was discovered that this glassy earth undergoes no alteration when heated by itself, but that when brought in contact with certain other bodies, it can be made to form a fusible glass. This substance was for a long time supposed to be the essential principle of all earths, but it was found that it differed from them inasmuch as it had no power of neutralising acids; and Tachenius, in the year 1660, noticed that it possessed acid rather than alkaline properties, since it combined with alkalis. The true nature of silica was then unknown, but Lavoisier, in his chemical nomenclature, anticipates that the time may probably soon arrive when this substance will be recognised as a compound body. After Davy's discovery of the compound nature of the alkalis and alkaline earths in the year 1808, silica, which was then classed amongst the earths, was supposed to possess a similar constitution.

In 1808 Berzelius prepared a substance which he regarded as impure silicon by fusing together iron, carbon, and silica, but the body he obtained was probably a compound of silicon and iron; whilst Gay-Lussac and Thénard[1] in 1811 obtained a brown amorphous powder, which we now know to be amorphous silicon, by passing the vapour of silicon tetrafluoride over heated potassium; they did not, however, determine the true nature of the body. Later, in 1823, the preparation of this

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[1] **Recherches physico-chimiques, 1811, I. 313: II. 53.**

element was described by Berzelius[1] as follows: dry potassium silico-fluoride is heated with metallic potassium to redness in an iron tube, when the following decomposition takes place:

$$K_2SiF_6+4K=6KF+Si.$$

On removing the potassium fluoride by treatment of the cooled mass with water, silicon is left as an amorphous brown powder. This has since been shown to be a very impure substance.[2]

Amorphous silicon has also been obtained by passing silicon tetrachloride through a red-hot tube over sodium.[3]

Pure silicon may best be prepared[4] by heating a mixture of powdered quartz and magnesium, in the calculated quantities with a quarter of its weight of calcined magnesia in a fire-clay crucible, first at 300° to 400° in order thoroughly to dry the material, and then for a few minutes at a red heat, when a vigorous reaction takes place according to the equation

$$SiO_2+2Mg=Si+2MgO.$$

After the action has ceased, the cooled mass is treated with hydrochloric acid to dissolve out the magnesia, then warmed several times alternately with hydrofluoric and sulphuric acids to remove unchanged silica, finally washed with water and dried by heating in a stream of dry hydrogen. By employing precipitated silica and pure magnesium a very pure form of silicon may be obtained. An impure form, which may be advantageously used for the preparation of many of its derivatives, can be rapidly obtained by heating 40 grm. of dry powdered white sand with 10 grm. of magnesium powder in a wide test-tube. The reaction is a tolerably vigorous one, and if carried out with precipitated silica is accompanied by a brilliant flash of light.[5]

Pure silicon prepared as above is an amorphous maroon-coloured powder, having a specific gravity of 2·35 at 15° (Vigouroux). When heated in air it oxidises superficially, and it takes fire in oxygen at about 400°, burning brilliantly to silica, whilst it decomposes steam slowly at a dull red heat forming silica and hydrogen.

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[1] *Pogg. Ann.* 1824, **1**, 169.

[2] Vigouroux, *Ann. Chim. Phys.*, 1897, [7], **12**, 5, where a historical account of the preparation of silicon is to be found.

[3] Deville, *Ann Chim. Phys.*, 1857, [3], **49**, 68.

[4] Vigouroux, *loc. cit.*

[5] Gattermann, *Ber.*, 1889, **22**, 186.

Acids, with the exception of a mixture of hydrofluoric and nitric acids, have no action upon it, but solutions of alkali hydroxides attack it in the cold with formation of an alkali metasilicate and evolution of hydrogen, thus:

$$Si + 2KOH + H_2O = K_2SiO_3 + 2H_2.$$

When heated in the electric furnace it readily fuses and volatilises.[1]

Amorphous silicon dissolves in many molten metals, uniting with the metal in some cases, as with iron, nickel, magnesium, copper, &c., to form metallic silicides, whilst in other cases, as, for example, with aluminium, zinc, and silver, no combination takes place, but on cooling the mass, silicon separates out in the crystalline form.[2]

A different variety of amorphous silicon, which possesses remarkable reducing properties, is obtained, according to Moissan and Smiles,[3] when sparks are passed through liquid silico-ethane; the silicon, prepared in this way, reduces neutral solutions of potassium permanganate in the cold, and copper sulphate, gold and mercuric chlorides on boiling.

Silicon may also be obtained crystalline either in six-sided plates or long needles, and these forms are sometimes distinguished as graphitoidal and adamantine silicon. The crystals of both forms are made up of regular octahedra, and they do not differ markedly in either physical or chemical properties. The crystalline modification of silicon is prepared by heating metallic aluminium to redness with three times its weight of potassium silico-fluoride in a fire-clay crucible, for about half-an-hour, when the following reaction takes place:

$$3K_2SiF_6 + 4Al = 6KF + 4AlF_3 + 3Si.$$

The temperature is then raised to about 1,000° and the silicon dissolves in the excess of aluminium, and on cooling crystallises out in thin plates, which are separated from the aluminium and potassium fluorides by washing with hydrochloric and hydrofluoric acids.[4]

Crystalline silicon can also be prepared by passing a slow

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[1] Moissan, *Compt. Rend.*, 1893, **116**, 1429.

[2] Vigouroux, *Compt. Rend.*, 1896, **123**, 115; *Ann. Chim. Phys.* 1897, [7], **12**, 153.

[3] *Compt. Rend.*, 1902, **134**, 1552.

[4] Wöhler, *Annalen*, 1856, **97**, 266; Vigouroux, *loc. cit.*

current of silicon tetrachloride over aluminium previously melted in an atmosphere of hydrogen:—

$$3SiCl_4 + 4Al = 4AlCl_3 + 3Si.$$

The silicon formed dissolves in the excess of fused aluminium until the metal is saturated with it, and on cooling, the silicon separates out in the crystalline form. It may also be prepared by throwing a mixture of thirty parts of potassium silicofluoride, forty parts of granulated zinc, and eight parts of finely-divided sodium into a red hot crucible, which is kept for some time at a heat just below the boiling-point of zinc. The regulus is then treated successively with hydrochloric acid, boiling nitric acid, and hydrofluoric acid, when dark glittering octahedral crystals are found to remain behind. If the temperature be raised above the boiling-point of zinc, the silicon melts and may be cast in sticks.[1]

Another method for the preparation of crystalline silicon consists in heating finely-powdered quartz with excess of aluminium in the electric furnace, and treating the cooled mass as before with acids, the silicon being left in thin plates (Vigouroux).

In all these methods of preparation, amorphous silicon is first formed, and this then dissolves in the excess of molten metal, from which it crystallises on cooling, from aluminium in the form of thin six-sided plates, and from zinc in needles (Vigouroux). Amorphous silicon is produced at a red heat, whilst a temperature of nearly 1,000° is required to bring about the solution of this substance in the metal.

A convenient way of preparing silicon in the crystalline form is to heat a mixture of powdered quartz, aluminium turnings and sulphur, the aluminium sulphide being decomposed by treatment of the cooled mass with water.[2]

If the vapour of silicon tetrachloride be passed through a porcelain tube containing silicon heated to redness, that substance becomes denser and assumes a light iron-grey colour. In this process a portion of the silicon appears to be volatilised, inasmuch as needle-shaped crystals are found in the further portion of the tube, the formation of which may be due to the production and decomposition of a lower chloride.

Crystalline silicon is formed from the amorphous variety by fusion, the change being accompanied by the evolution of 8,059

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[1] *Ann. Chim. Phys.*, 1861, [3], **63**, 26; 1863, [3], **67**, 435.

[2] Kühne, German Patent 147, 871.

units of heat per atom,[1] or by sublimation in a carbon tube heated in the electric furnace (Vigouroux).

Crystalline silicon prepared by the foregoing methods is transparent and of a light orange-yellow colour when the crystals are small, but when massed together, or in large crystals, it has an opaque, metallic appearance (Vigouroux).[2] It has a specific gravity of 2·49 (Wöhler), and does not differ from the amorphous variety in its chemical properties. The specific heat of silicon varies with the temperature considerably, but becomes constant at about 232°, and is then equal to 0·203, whilst at 22° it is 0·1697 (Weber).[3]

If silicon be dissolved in fused silver, it separates out on cooling in the ordinary crystalline form, mixed with a modification, also crystalline, and having a specific gravity of 2·42, which differs from the ordinary variety in that it is soluble in hydrofluoric acid.[4]

Crystalline silicon can be produced on the large scale by heating silica in an electric furnace with carbon, in amount insufficient to form carborundum, with or without a flux.[5] The silicon is obtained in lumps of metallic appearance and is used as a deoxidiser for castings of steel, copper or bronze.

The Atomic Weight of Silicon.—Berzelius determined the atomic weight of silicon by the oxidation of the element and by the analysis of barium silico-fluoride, but did not obtain satisfactory results. The analysis of the chloride carried out by Dumas and Schiel led to the value 27·9, whilst Pelouze obtained a slightly higher number; finally, the conversion of the bromide into the oxide by decomposition with water has given the number 28·2[6] (H = 1), whilst Becker and Meyer[7] by converting the chloride into the oxide by means of water have obtained the lower number 27·99 (H = 1).

The most probable value is at present (1905) taken as 28·2 (H = 1).

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[1] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [5], **9**, 76.

[2] Warren, *Chem. News*, 1893, **67**, 136.

[3] *Pogg. Ann.*, 1875, **154**, 367.

[4] Moissan and Smiles, *Compt. Rend.*, 1904, **138**, 1299.

[5] Scheid, Brit. Patent, No. 18,659 of 1899; Tone, U.S.A. Patent, No. 745, 122 of 1903.

[6] Thorpe and Young, *Journ. Chem. Soc.*, 1887, 576.

[7] *Zeit. anorg. Chem.*, 1905, **43**, 251.

SILICON AND HYDROGEN.

SILICON TETRAHYDRIDE OR SILICO-METHANE, SiH_4.

509 This substance, which was discovered by Buff and Wöhler in 1857, is obtained by acting with hydrochloric acid upon an alloy of silicon and magnesium, prepared by fusing together forty parts of anhydrous magnesium chloride with a mixture of thirty-five parts of sodium silico-fluoride, ten parts of common salt, and twenty parts of sodium. The dark-coloured mass which is thus obtained evolves silicon hydride when brought in contact with acidulated water. For this purpose the magnesium silicide is brought into the bottle (Fig. 207), and the latter then completely filled with cold water from which all the air has been expelled by boiling. A wide gas-delivery tube, also completely filled with the same water, is connected with the bottle, and hydrochloric acid is poured down a funnel tube passing through the cork to the bottom of the bottle. The evolution soon begins, and the gas must be collected over water free from air. Every bubble of the gas thus obtained takes fire spontaneously when brought in contact with the air, burning brilliantly with formation of a cloud of silica, which escapes in the form of a ring similar to that produced by phosphine. If a jar be filled with the gas over water, and then opened in the air, the gas also takes fire spontaneously, burning with a luminous flame and depositing a brown film of amorphous silicon in consequence of the limited supply of oxygen. The gas thus prepared always contains free hydrogen, and this depends, according to Wöhler, upon the fact that the black mass contains two magnesium compounds, by the decomposition of one of which

FIG. 207.

the pure silicon hydride is evolved, whilst the other yields hydrogen and hydrated silica.

The gas may also be obtained by passing silicon fluoride over heated magnesium and then treating the mass with acids,[1] but when prepared by this and the preceding method, it contains some silico-ethane.

Silicon and hydrogen have been made to combine to a slight extent to form silico-methane, by passing dry hydrogen over silicon heated in the electric arc.[2]

Pure silico-methane can be obtained by acting with sodium on triethyl silicoformate (Friedel and Ladenburg).[3] In this reaction ethyl silicate and silico-methane are formed, thus:—

$$4Si(OC_2H_5)_3H = 3Si(OC_2H_5)_4 + SiH_4.$$

The sodium employed in this reaction remains unacted on, and the part it plays is not understood. The colourless gas thus obtained does not take fire at the ordinary temperature, but it does so when slightly warmed or when mixed with hydrogen. If the gas be collected over mercury and the bubbles as they emerge from the surface of the mercury be brought in contact with a heated knife-blade, they take fire, and the mercury soon becomes sufficiently heated to enable the bubbles to take fire spontaneously. Silicon hydride decomposes at a red heat into amorphous silicon and hydrogen, the volume of the hydrogen gas being twice that of the compound gas taken, and when the gas is passed through a heated narrow tube an opaque mirror of silicon is deposited. When decomposed with caustic potash, one volume of the gas yields four volumes of hydrogen:—

$$SiH_4 + H_2O + 2KOH = K_2SiO_3 + 4H_2.$$

Silicon hydride takes fire when brought into chlorine gas, with formation of silicon tetrachloride and hydrochloric acid. It condenses to a liquid under a pressure of 100 atmospheres at −1°, of 70 atmospheres at −7°, and of 50 atmospheres at −11°; its critical temperature is probably about 0°,[4] and its boiling point[5] −115° to −116° at 730 mm.

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[1] Warren, *Chem. News*, 1888, **58**, 210.

[2] Dufour, *Compt. Rend.*, 1904, **138**, 1040; Vigouroux, *Compt. Rend.*, 1904, **138**, 1168.

[3] *Annalen*, 1867, **143**, 124.

[4] Ogier, *Compt. Rend.*, 1879, **88**, 236.

[5] Dufour, *Compt. Rend.*, 1904, **138**, 1040.

When silicon hydride is submitted to the action of the electric current a yellow substance of the formula Si_2H_3 is deposited, which burns when heated in the air or in chlorine.[1]

SILICON HEXAHYDRIDE OR SILICO-ETHANE, Si_2H_6.

510 This compound was obtained by Moissan and Smiles [2] by the action of hydrochloric acid on magnesium silicide, prepared by heating magnesium and silicon together in the proportion of two atoms of the former to one of the latter, and by passing the mixture of hydrogen, silico-methane and silico-ethane evolved through tubes cooled by liquid air. The silicon hydrides solidified, and the silico-ethane was obtained from this solid by fractional volatilisation, as a colourless liquid.

It is also formed by the action of concentrated hydrochloric acid on lithium silicide, Li_6Si_2, prepared by heating lithium with amorphous silicon to redness for a few hours in a vacuum, and may be collected in a receiver cooled by liquid air.[3]

Silico-ethane is a mobile, colourless liquid, which boils at 52° and, when solidified by liquid air, melts at $-138°$; the vapour takes fire spontaneously on exposure to air, rapid and even explosive combination taking place with formation of silica and water; when dried by sulphuric acid, the explosive nature of the combination is increased; it is decomposed into its elements on heating to 250°.

The vapour density at 100° was found by Gay-Lussac's method to be 2·37 corresponding with the formula Si_2H_6 (Moissan). It dissolves sparingly in water, the solution being slowly oxidised, and reduces solutions of mercuric chloride, auric chloride, silver nitrate, potassium permanganate and many other salts; whilst solutions of the alkali hydroxides are attacked with formation of hydrogen and alkali silicates.

A violent explosion occurs when silico-ethane is mixed with carbon tetrachloride, with formation of hydrogen chloride, carbon and silicon; it also explodes when mixed with sulphur hexafluoride, silicon being deposited.

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[1] Ogier, *Compt. Rend.*, 1879, **89**, 1068.

[2] *Compt. Rend.*, 1902, **134**, 569, 1549.

[3] Moissan, *Compt. Rend.*, 1902, **134**, 1083; 1903, **135**, 1284.

SILICON AND THE HALOGENS.

511 *Silicon Tetrafluoride*, SiF_4.—This gas was first observed by Scheele in the year 1771. It was also obtained by Priestley, and was afterwards examined by Gay-Lussac and Thénard in 1808, and by J. Davy in 1812. We are, however, indebted to Berzelius for the most accurate investigation of this compound, carried out in the year 1823.[1]

In order to prepare this gas, white sand or powdered glass is heated with fluor-spar and concentrated sulphuric acid:

$$2CaF_2 + 2H_2SO_4 + SiO_2 = SiF_4 + 2CaSO_4 + 2H_2O.$$

In this operation it is necessary that an excess of sulphuric acid should be employed in order to absorb the water which is formed in the reaction and which would otherwise decompose the gas.[2]

Silicon tetrafluoride may be formed by direct combination of the elements, amorphous silicon being attacked by fluorine with incandescence and formation of the tetrafluoride.[3]

Silicon tetrafluoride is a colourless gas, fuming strongly in the air, possessing a highly pungent odour like that of hydrochloric acid, and condensing to a colourless liquid. It solidifies at $-97°$ under atmospheric pressure, and volatilises without liquefying under a pressure of 2 atmospheres. It melts at $-77°$ to a transparent mobile liquid, which boils at $-65°$ under 181 cm. pressure; the critical temperature is $-1·5°$ and the critical pressure 50 atmospheres.[4] The specific gravity of the gas according to the experiments of J. Davy is 3·57. It is incombustible, and is decomposed by water with separation of gelatinous silica. Fused sodium takes fire when brought into the gas and burns with a red flame. Dry ammonia combines with the gas, forming a white crystalline body, having the composition $SiF_4 2NH_3$, which is decomposed by water. Three volumes of the gas unite with two of phosphine at $-22°$ and 53 atmospheres to form lustrous crystals of an unstable compound.[5]

512 *Silico-fluoric, Fluosilicic or Hydrofluosilicic Acid*, H_2SiF_6.

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[1] *Pogg. Ann.*, 1824, **1**, 169.
[2] Faraday, *Phil. Trans.*, 1845, 155.
[3] Vigouroux, *Compt. Rend.*, 1895, **120**, 367.
[4] Moissan, *Compt. Rend.*, 1904, **139**, 711.
[5] Besson, *Compt. Rend.*, 1890, **110**, 80.

When silicon tetrafluoride is led into water the following decomposition takes place:—

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4.$$

The silicic acid separates out in the form of a gelatinous mass, and in order to prevent the gas delivery-tube, by which the tetrafluoride is passed into the water, from becoming stopped up, the end of this tube is allowed to dip under mercury as seen in Fig. 208. As soon as the mass begins to become thick it must be frequently stirred up, otherwise channels are formed through which the gas can escape into the air without coming into contact with the liquid. The thick jelly is pressed in a linen filter and the filtrate concentrated at a low temperature. The same acid is formed when silica is dissolved in hydrofluoric acid, and also when silicon fluoride is passed into concentrated hydrofluoric acid, the solution in this case depositing crystals of the formula $H_2SiF_6 + 2H_2O$,[1] which melt at 19°. The saturated solution forms a very acid, fuming, colourless liquid, which may be evaporated down in platinum vessels without leaving any residue, as, on boiling, it decomposes into silicon tetrafluoride and hydrofluoric acid. The

FIG. 208.

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[1] Kessler, *Compt. Rend.*, 1880, **90**, 1285,

specific gravity of the aqueous hydrofluosilicic acid is seen in the following table[1]:—

Per cent.	Specific gravity.	Per cent.	Specific gravity.
0·5	1·0040	10	1·0834
1·0	1·0080	15	1·1281
1·5	1·0120	20	1·1748
2·0	1·0161	25	1·2235
5·0	1·0407	30	1·2742

This acid forms salts which are termed the silico-fluorides. Most of these are soluble in water, the exceptions being the lithium salt, Li_2SiF_6, the sodium salt, Na_2SiF_6, the potassium salt, K_2SiF_6, the barium salt, $BaSiF_6$, the calcium salt, $CaSiF_6$, and the yttrium salt, $YSiF_6$, which are more or less sparingly soluble. One part of the barium salt dissolves in 3,802 parts of cold water.[2] Hence this acid is used as a re-agent for barium salts and for the separation of this metal from strontium. The soluble silico-fluorides possess an acid reaction, and a bitter taste. They all decompose on heating in the air yielding a fluoride and a silicate.

A subfluoride of silicon, the exact composition of which is unknown, is said to be formed when silicon fluoride is passed over melted silicon and then suddenly cooled. It is deposited as a white volatile powder, which contains less fluorine than the tetrafluoride and reduces potassium permanganate solution.[3]

Silico-fluoroform or *Trifluorosilico-methane*, $SiHF_3$, is obtained by the action of titanium tetrafluoride on silico-chloroform (p. 886) at 100°, the chlorine in the latter being thereby replaced by fluorine. It is a colourless gas, which condenses to a liquid boiling at −80°, and on further cooling solidifies to a solid melting at −110°. It burns in the air with a very pale bluish flame and decomposes on heating to about 420° into silicon fluoride, silicon and hydrogen, whilst with water it yields silicic acid and hydrofluosilicic acid with evolution of hydrogen. Caustic alkalis effect a similar decomposition.[4]

$$2SiHF_3 + 4H_2O = Si(OH)_4 + H_2SiF_6 + 2H_2.$$

513 *Silicon Tetrachloride*, $SiCl_4$.—This compound, discovered by Berzelius in the year 1823, is prepared by the direct union

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[1] Stolba, *J. pr. Chem.*, 1863, [1], **90**, 193.
[2] Fresenius, *Annalen*, 1846, **59**, 120.
[3] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [5], **7**, 463.
[4] Ruff and Albert, *Ber.*, 1905, **38**, 53.

of its elements, or by passing a current of dry chlorine over a strongly heated mixture of silica and charcoal, obtained by mixing silica and oil in the form of small balls, igniting these in a covered crucible, and then placing them in a porcelain tube (*a b* Fig. 209) heated to whiteness. The reaction which takes place is as follows:—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

The escaping vapours and gases pass through an absorption tube (*c*) surrounded by a freezing mixture, and the product is separated from absorbed chlorine by shaking with metallic mercury and subsequent distillation.

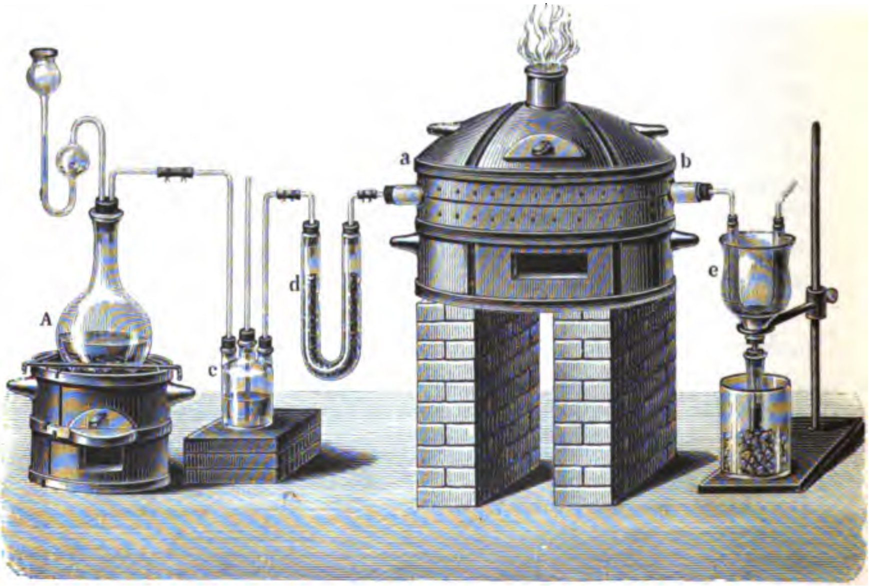

FIG. 209.

It may be readily prepared by passing chlorine over the mass of crude silicon obtained by Gattermann's method (p. 874), heated at 300—310°, when it is obtained mixed with a little of the hexa- and octochlorides, from which it may be separated by fractional distillation. It may also be prepared by passing chlorine over an alloy of iron containing 15 per cent. of silicon (siliconeisen) heated to redness in a fire-clay retort, the less volatile ferric chloride being retained in a suitable adapter, and the silicon tetrachloride condensed in a receiver cooled by a freezing mixture.[1]

Silicon tetrachloride is an acrid colourless liquid, fuming in the air, having a specific gravity at 0° of 1·52408 and boiling at 59·57° (Thorpe). The specific gravity of its vapour, according to Dumas, is 5·937. When thrown into water, silicon tetrachloride is at once decomposed, hydrochloric and silicic acids being formed, and the latter deposited as a gelatinous mass.

It reacts with six molecules of ammonia to form a white amorphous mass (see p. 902), and forms an unstable crystalline compound when compressed with phosphine at a low temperature.[2]

Silicon Trichloride, Si_2Cl_6.—Friedel obtained this compound, along with a small quantity of spontaneously inflammable liquid[3] which probably has the composition $SiCl_2$, by gently heating the corresponding tri-iodide with mercuric chloride.[4] The same compound was obtained by Troost and Hautefeuille[5] by passing the vapour of silicon tetrachloride over silicon heated in a porcelain tube to whiteness, and by Gattermann and Weinlig as a secondary product in the preparation of the tetrachloride from crude silicon, the mixed chlorides being separated by fractional distillation.[6] It is a colourless liquid solidifying at −1° and boiling at 146°, having a specific gravity at 0° of 1·58. The specific gravity of its vapour is 9·7. It fumes strongly in the air, takes fire on heating, and is decomposed by cold water with formation of silico-oxalic acid, $H_2Si_2O_4$ (Gattermann and Weinlig). At a temperature of 350° the vapour begins to decompose, and the amount of decomposition increases with the temperature up to 800°, when it is completely dissociated into the tetrachloride and silicon.

If the temperature of the vapour be quickly raised beyond 1,000° no such dissociation is, on the contrary, observed. We have, therefore, here to do with a substance possessing the remarkable property of being stable at temperatures below 350° and above 1,000°, and dissociating at intermediate temperatures. This explains the singular fact observed by Troost and Hautefeuille, that if the vapour of silicon tetrachloride be passed

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[1] Warren, *Chem. News*, 1892, **66**, 113.

[2] Besson, *Compt. Rend.*, 1890, **110**, 240.

[3] *Annalen*, 1880, **203**, 254.

[4] *Compt. Rend.*, 1871, **73**, 1011.

[5] *Ann. Chim. Phys.*, 1876, [5], **7**, 461.

[6] *Ber.*, 1894, **27**, 1943.

over silicon heated to above 1,000° in a porcelain tube, the silicon is transported from the heated to the cooled part of the tube. This is not due simply to the volatilisation of the silicon, for no such change is observed when this body is heated in an atmosphere of hydrogen, but is to be explained by the alternate formation (at a high temperature) and dissociation (at a lower temperature) of the trichloride.

It unites with ten molecules of ammonia to form a white substance which loses ammonia at 100°. Phosphine is immediately reduced by it with formation of solid hydrogen phosphide.[1]

Silicon Octochloride, Si_3Cl_8, is also formed by the action of chlorine on crude silicon, and is obtained from the residue after the fractional distillation of the trichloride.[2] The production of this body seems to depend upon the presence of magnesium silicide in the crude silicon, for if none of this be present little or no octochloride is formed.[3] Silicon octochloride is a colourless liquid boiling at 210—215°, and having a vapour density corresponding with the formula Si_3Cl_8. Cold water decomposes it with formation of an insoluble acid, $H_4Si_3O_6$, which will be described later.

Silico-chloroform or Trichlorosilico-methane, $SiHCl_3$.—This body was first obtained in the impure state by Wöhler and Buff by heating silicon in a current of dry hydrochloric acid gas at a temperature just below red heat, and may readily be prepared in this way at a temperature of 450—500° from the crude silicon obtained by Gattermann's method (p. 874). In order to prepare the pure compound, the crude product thus obtained is condensed in a tube surrounded by a freezing mixture, and the silico-chloroform separated by subsequent distillation from the tetrachloride formed at the same time. It is a colourless, mobile, strongly-smelling liquid, which fumes on exposure to the air and boils at 34°. It is very inflammable, and burns with a green mantled flame, evolving white clouds of silica. When a hot glass rod is brought into a mixture of this body and air, the mixture burns with explosion (Gattermann). Water readily decomposes it in the cold, a white powder being precipitated to which the name *silico-formic anhydride*, $Si_2H_2O_3$, has been given (Friedel and Ladenburg).

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[1] Besson, *Compt. Rend.*, 1890, **110**, 516.

[2] Gattermann and Weinlig, *Ber.*, 1894, **27**, 1943.

[3] Gattermann and Ellery, *Ber.*, 1899, **32**, 1114.

Silicon Tetrabromide, $SiBr_4$.—This compound, discovered in the year 1831 by Serullas,[1] is obtained by reactions similar to those employed for the preparation of the chloride.[2] It is generally prepared directly from crude silicon, which is heated in a current of bromine vapour (Gattermann).

The tetrabromide is a colourless heavy liquid, having a specific gravity of 2·813, boiling at 150·8° under 751·4 mm. pressure, and solidifying to a crystalline mass, melting at 5°.[3] When brought in contact with water it is decomposed into hydrobromic and silicic acids.

With ammonia it forms a white amorphous compound, $SiBr_4 + 7NH_3$, which is decomposed by water; and with phosphine it seems to form an unstable compound at a high pressure.[4]

Silicon Tribromide, Si_2Br_6.—This colourless and crystalline compound is formed when the corresponding iodine compound is treated with bromine in the presence of carbon bisulphide. Large crystalline tablets are formed, which melt on heating, and may be distilled at 240° without undergoing decomposition.[5]

Silico-bromoform, $SiHBr_3$, is formed by the action of hydrogen bromide on silicon,[6] and may be prepared in this way from crude silicon (Gattermann).

It boils at 115—117° (Gattermann),[7] 109—111° (Besson),[8] and is spontaneously inflammable in the air. In its chemical relationships it resembles silico-chloroform.

Silicon Tetra-iodide, SiI_4.—Friedel obtained the tetra-iodide by the direct combination of the two elements. For this purpose he volatilised iodine in a stream of dry carbon dioxide, and led the mixed gases over heated silicon[9]; the iodide may also be prepared in this way from crude silicon (Gattermann).

The tetra-iodide is a colourless crystalline mass which is deposited in the form of regular octahedra from solution in carbon bisulphide. Its melting-point is 120·5° and its boiling-

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[1] *Ann. Chim. Phys.*, 1831, [2], **48**, 87.

[2] Reynolds, *Journ. Chem. Soc.*, 1887, 590.

[3] Blix, *Ber.*, 1903, **36**, 4218.

[4] Besson, *Compt. Rend.*, 1890, **110**, 240.

[5] Friedel and Ladenburg, *Annalen*, 1880, **203**, 253.

[6] Wöhler and Buff, *Annalen*, 1857, **104**, 99.

[7] *Ber.*, 1889, **22**, 193.

[8] *Compt. Rend.*, 1891, **112**, 530.

[9] *Annalen*, 1869, **149**, 96.

point 290°. Heated in the air it takes fire and burns with a reddish flame. It is decomposed in presence of water into hydriodic and silicic acids.

Silicon Tri-iodide, Si_2I_6, was likewise first obtained by Friedel and Ladenburg[1] by heating the tetra-iodide with finely-divided silver to a temperature of 280°:

$$2SiI_4 + 2Ag = Si_2I_6 + 2AgI.$$

It crystallises from carbon bisulphide in splendid colourless hexagonal prisms or rhombohedra, which fume on exposure to the air, and, owing to the absorption of moisture, change to a white mass with formation of silicic and hydriodic acids. It melts when heated, but decomposes with the formation of SiI_4 and a lower iodide, and is attacked by ice-cold water with formation of silico-oxalic acid, unaccompanied by evolution of hydrogen.

Silico-iodoform, $SiHI_3$.—For the purpose of preparing this compound, a mixture of hydrogen and hydriodic acid is passed over silicon heated just to redness. It is a colourless strongly-refractive liquid boiling at 220° and having a specific gravity at 0° of 3·362. It is decomposed by water in a manner corresponding to the chlorine compound (Friedel).

MIXED HALOGEN DERIVATIVES OF SILICON.

514 When a mixture of hydrogen bromide with silicon chloride vapour is passed through a red-hot glass tube, a mixture of the chlorobromides of silicon is formed.[2] *Bromo-trichlorosilico-methane*, $SiCl_3Br$, is also formed by the action of bromine on silico-chloroform at 100°, or on silicon chlorosulphide at the ordinary temperature.[3]

The chloro-iodides and bromo-iodides of silicon are obtained by similar reactions. They are all decomposed by water and form solid compounds with ammonia, which, however, may be mixtures of silicon di-imide, $Si(NH)_2$, and haloid salts of ammonia. Their physical properties are given in the annexed table:—

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[1] *Annalen*, 1880, **203**, 247.

[2] Besson, *Compt. Rend.*, 1891, **112**, 788.

[3] Friedel, *Annalen*, 1867, **143**, 118; 1868, **145**, 185.

Formula.	Boiling-point.	Melting-point.	Combines with
$SiCl_3Br$ . .	80°	—	$5{\cdot}5NH_3$
$SiCl_2Br_2$ . .	103°—105°	—	$5\ NH_3$
[1] $SiClBr_3$ . .	126°—128° (B) 140°—141° (R)	−39°	$11\ NH_3$
[2] $SiCl_3I$ . .	113°—114°	—	$5{\cdot}5NH_3$
[2] $SiCl_2I_2$ . .	172°	—	$5\ NH_3$
[2] $SiClI_3$ . . .	234°—237°	2°	—
[3] $SiBr_3I$ . . .	192°	14°	—
[3] $SiBr_2I_2$ . .	230°—231°	38°	—
[3] $SiBrI_3$ . .	255°	53°	—

SILICON AND OXYGEN.

SILICON DIOXIDE OR SILICA, $SiO_2 = 59{\cdot}96$.

515 Silicon forms only this one oxide, which is an extremely important constituent of our planet. It is found not only in the mineral but also in the vegetable and animal kingdoms, existing in large quantity in the glassy straw of the cereals and of bamboos, and in the feathers of certain birds, which have been found to contain as much as 40 per cent. of this substance, whilst silicic acid has been found in all forms of connective tissue.[4] Vast deposits of pure silica in a very fine state of division occur in various parts of Germany, especially in Hanover and near Berlin. This consists of the skeletons of extinct diatomaceæ, and is termed *kiesel-guhr*. Large quantities of this substance are now used for a variety of purposes, especially for the preparation of dynamite, for filtering, and as a non-conducting medium for packing steam-pipes. The minute and beautifully-formed spicules of the spongidæ and radiolariæ also consist of pure silica.[5] In the mineral kingdom it is found in three distinct forms:—

(*a*) *Quartz* is the most important form of silica. It crystallises in the hexagonal system (trigonal holoaxial),

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[1] Reynolds, *Journ. Chem. Soc.*, 1887, 590.

[2] Besson, *Compt. Rend.* 1891, **112**, 611, 1314.

[3] Friedel, *Ber.*, 1869, **2**, 60.

[4] Schulz, *Pflüger's Arch.*, 1901, **84**, 67; 1902, **34**, 455.

[5] Besson, *Compt. Rend.* 1891, **112**, 1447.

forming usually combinations of the prism with the rhombohedron; three of the most usual forms are shown in Figs. 210, 211, and 212. The relation of its axes is 1·0999 : 1. It has a specific gravity of 2·65 and a hardness of 7. The purest form of quartz is known as rock crystal. It is usually colourless and transparent. Sometimes, however, quartz is coloured by the presence of traces of oxides of manganese, which give it a violet tint, and it is then termed amethyst quartz. Other varieties containing more or less impurity are known as milk quartz, rose quartz, and smoky quartz. Crystalline quartz also occurs in large masses, forming whole mountain ranges as quartzose rock. It forms one of the chief constituents of granite, gneiss, and syenite, whilst sand and sandstone consist of an impure variety of quartz.

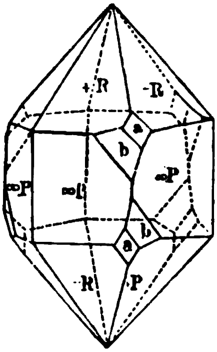

FIG. 210.

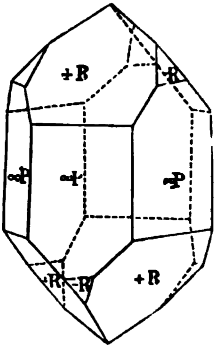

FIG. 211.

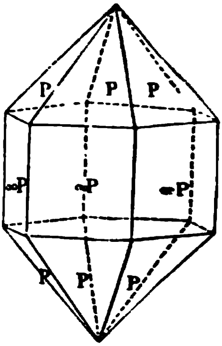

FIG. 212.

(*b*) *Tridymite* is a second crystalline variety of silica discovered by G. v. Rath[1] in the trachytic porphyry found at Pachuca in Mexico. This form of silica occurs in many other similar rocks, and is found in considerable quantity in the trachyte of Stenzelberg in the Siebengebirge. Tridymite crystallises in the triclinic[2] system, and forms six-sided tablets, which are combinations of a prism with pyramids, Fig. 213. The

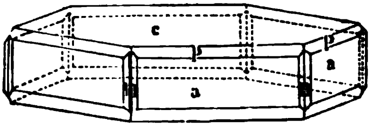

FIG. 213.

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[1] *Pogg. Ann.*, 1868, **133**, 507, and 1868, **135**, 437.

[2] Lasaulx, *Jahrb. Min.*, 1878, p. 408.

ratio of the axes is 0·5812 : 1 : 1·1040, and the whole form approaches very closely to one belonging to the rhombic system in which it has been placed by some investigators. It has the specific gravity 2·3, and the same hardness as quartz. A very characteristic property of this mineral is that it generally occurs in *trillings* or triplets (Fig. 214), from which its name has been derived. These are generally found grown together in twinned groups, as in Fig. 215.

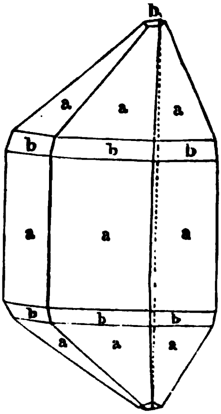

FIG. 214.

Identical with tridymite is the mineral asmanite which has been found in certain meteorites.

(*c*) *Amorphous Silica* occurs in nature containing more or less water as *opal*. This substance is either colourless or variously coloured, possesses a vitreous fracture, and has a specific gravity of 2·2. It not unfrequently happens that crystals of tridymite are found in the non-transparent portions of this opal, and

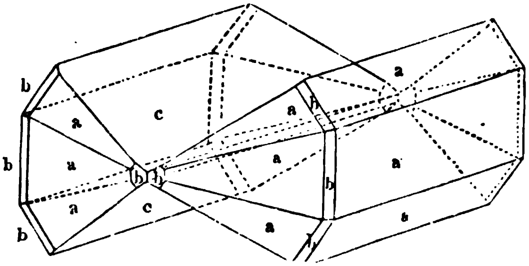

FIG. 215.

these remain as an insoluble residue when the opal is treated with caustic potash (G. Rose). *Chalcedony*, *agate*, and *flint* are intimate mixtures of amorphous silica with quartz or tridymite.

Hydrated amorphous silica is formed by passing silicon tetrafluoride into water. When the gelatinous mass is washed with water, dried, and ignited, pure finely divided amorphous silica remains behind as a white very mobile powder. Amorphous silica may be obtained in the same form by decomposing a silicate of an alkali metal with an acid. For this purpose one part of quartz, flint, or white sand, is fused with four parts of sodium carbonate. If flint or quartz be employed it must previously be reduced to powder, and this is easily effected by heating the mass to redness and then quickly plunging it into cold water, after which it becomes friable and can readily be powdered. The fused mass is then heated with hydrochloric acid, when it becomes gelatinous, an alkali chloride and silicic acid being formed. The gelatinous mass is afterwards evaporated to dryness on the water-bath, and the residue moistened with strong hydrochloric acid, in order to dissolve any oxide of iron or other oxides, whilst the silica remains undissolved in the anhydrous state as a light white powder, which only requires washing and drying to render it perfectly pure. Amorphous silica has a specific gravity of 2·2. If, however, it be heated strongly for a long time its specific gravity increases, inasmuch as it is then transformed into tridymite.[1] Rock crystal undergoes the same change when the perfectly pure material is finely powdered and heated to 2,000°, its specific gravity diminishing from 2·6 to 2·3.[2]

Silica melts in the oxy-hydrogen flame to a colourless glass which may be drawn out in threads. It slowly volatilises when maintained at a high temperature in a wind furnace[3] for some time, and can readily be made to boil when heated in the electric furnace.[4]

Quartz glass, obtained by fusing silica in the electric furnace, has the lowest coefficient of expansion for heat of any known substance, the mean coefficient between 0° and 1,000° being

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[1] Rammelsberg, *Ber.*, 1872, **5**, 1006.

[2] G. Rose, *Ber.*, 1869, **2**, 338.

[3] Cramer, *Zeit. angew. Chem.*, 1892, 484.

[4] Moissan, *Compt. Rend.*, 1893, **116**, 1122.

only 0·0000007.[1] When fragments of quartz, heated to 1,000°, are thrown into cold water, a white enamel-like product is obtained, which may be fused into rods, from which tubes and vessels may be constructed.[2] The glass made in this manner is much more transparent to the ultra-violet rays than ordinary glass, is unacted upon by water, and owing to its small coefficient of expansion with heat, possesses great stability towards sudden changes of temperature.

On account of these properties vessels made of fused quartz have been recommended for experiments in thermometry and at high temperatures; whilst threads made of very finely drawn out quartz have been used in galvanometers and in other instruments where very delicate suspensions are required (Boys).

In all three conditions silica is insoluble in water, and also in all acids except hydrofluoric, in which it readily dissolves. Crystallised silica is as a rule scarcely attacked by alkalis, whilst the amorphous form is soluble, especially when in a fine state of division, but loses this property to a large extent when ignited. The amorphous variety, especially if it contains water also dissolves in alkali carbonates. Hence silica is found in many spring waters, especially those of the hot Icelandic springs, which on exposure to air deposit this substance, the alkali silicates being decomposed by the atmospheric carbonic acid, while silica and an alkali carbonate are formed. The occurrence of silica in these springs was observed so long ago as 1794 by Black, but even before that date Bergman had shown that small quantities of silica were contained in solution in the water of many springs.

When an alkaline solution of silica is heated in a sealed tube the glass is attacked and an acid silicate is formed from which silica separates out on cooling. If the temperature at which the deposition occurs be above 180°, the silica separates out as quartz; if below this point, it crystallises out as tridymite; whilst at the ordinary temperature of the air it separates in the form of a hydrated amorphous mass.[3]

The various forms of silica are employed in a variety of technical processes, many of which will be hereafter described,

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[1] Le Chatelier, *Compt. Rend.*, 1900, **130**, 1703.

[2] Shenstone, *Proc. Roy. Inst.*, 1901.

[3] Maschke, *Pogg. Ann.*, 1872, **145**, 549; 1872, **146**, 90.

especially its application to the manufacture of glass and porcelain. The coloured varieties of silica are also largely used as gems and for other ornamental purposes. It is also possible to colour the natural agates artificially. Thus brown or yellow agates or chalcedonies when strongly heated are changed into ruby carnelians, the yellow oxide of iron being thereby changed into the red anhydrous oxide. Many agates and chalcedonies are permeable to liquids, and in this way they may be artificially coloured. This fact was known to the ancients and made use of in darkening the colour of agates. Thus Pliny states that in Arabia, agates occur which having been boiled in honey for seven days and nights become marked by veins, striæ or spots, and are thus rendered much more valuable as ornaments, the boiling in honey having the object of freeing them from all earthy and impure materials. Pliny was evidently only acquainted with half the mode of procedure, the object being to saturate the stone with honey, which by heating was carbonised, and thus brown or black streaks were produced. This process was kept very secret by the Roman lapidaries, and for centuries they came to the valley of the Nahe (where formerly rich agate-quarries existed, and which is still the chief seat of the agate industry) to buy up badly-coloured stones and to colour them at home. Not very long ago a tradesman from Idar was imprisoned in Paris for debt, and met there a "Romaner," who told him the secret, which consists of soaking the stones in sulphuric acid after they have been boiled in honey, the sugar being thus carbonised and the agate coloured dark.[1] Agate is also largely used for making the agate mortars so necessary for the chemist, and rock crystal is sometimes employed for preparing the unalterable weights which he uses in his most accurate investigations.

SILICIC ACID.

516 Silica belongs to the class of acid-forming oxides, and we should therefore expect the hydrated acid to have either the formula $Si(OH)_4$ or $SiO(OH)_2$.

Orthosilicic acid, $Si(OH)_4$, like sulphurous acid, H_2SO_3, and carbonic acid, H_2CO_3, appears to have a great tendency to

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[1] *Ber. über die Entw. Chem. Ind.*, p. 263.

split up into water and the acid-forming oxide. An acid stated to be orthosilicic acid has been prepared by treatment of the gelatinous mass, obtained by passing silicon tetrafluoride into water, first with benzene and then with absolute ether, and drying the powder formed by pressing between filter paper; in this way an amorphous white powder was obtained having the composition H_4SiO_4, which lost water rapidly on exposure to the air.[1]

If a solution of an alkali silicate, termed soluble glass, be acidified with hydrochloric acid, a portion of the silicic acid separates out as a gelatinous mass, whilst another portion remains in solution. If, on the other hand, the solution is sufficiently dilute, no precipitate will occur, all the silicic acid remaining dissolved. This liquid contains silicic acid, hydrochloric acid, and common salt in solution. In order to separate the last two compounds from the first, the liquid is brought into a flat drum, the bottom of which consists of parchment paper, and this "dialyser" containing the liquid is allowed to swim on the surface of a large volume of water. The sodium chloride and the excess of hydrochloric acid pass through the membrane, whilst a clear aqueous solution of silicic acid remains behind.

This mode of separation was termed "dialysis" by its discoverer, Graham.[2] This chemist first pointed out that substances which crystallise, hence termed "crystalloids," have as a rule the power of passing in solution through a membrane such as parchment or an animal membrane, whilst substances, such as gum and glue, which form jellies and are termed "colloids," are unable to pass through such a diaphragm or septum.[3]

A fluid mixture of a colloid and a liquid is termed a "sol," a watery mixture being called a "hydrosol," whilst a firm mixture of a colloid and a liquid is named a "gel," thus silicic acid jelly is a "hydrogel" of silicic acid.

These so-called colloidal solutions, which are thought by many workers to be suspensions and not true solutions, have the power of polarising transmitted light.

By dialysis an aqueous solution of pure silicic acid may be

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[1] Norton and Roth, *J. Amer. Chem. Soc.*, 1897, **19**, 832.

[2] *Phil. Trans.*, 1861, 204.

[3] Ostwald, *Lehrb. d. Allg. Chem.* (Leipzig, 1903), **1**, 702.

obtained which contains 5 per cent. of silica, and this may be concentrated by boiling it in a flask until it reaches a strength of 14 per cent. When heated in an open vessel, such as an evaporating basin, it is apt to gelatinise round the edge, after which the whole solidifies. The solution of silicic acid thus prepared has a feebly acid reaction and is colourless, limpid, and tasteless. On standing for a few days the solution gelatinises to a transparent jelly. This coagulation is retarded by the presence of a few drops of hydrochloric acid, or of caustic alkali, but it is brought about by even the smallest traces of an alkali carbonate.

If the clear solution be allowed to evaporate in a vacuum at 15° a transparent glass-like mass remains behind, which, when dried over sulphuric acid, possesses approximately the formula, $H_2SiO_3 = SiO_2 + H_2O$. This has been termed *metasilicic acid*, and an acid of the same composition has been obtained by dehydrating precipitated gelatinous silicic acid with 90 per cent. alcohol.[1]

By drying gelatinous silicic acid at the ordinary temperature, it was at one time supposed that hydrates of a constant composition could be obtained, and it was believed that the different kinds of opal, which usually contain water, consisted of hydrates of well-defined composition corresponding with the different hydrates of phosphoric acid. Further investigation, however, has shown that the quantity of water contained in the artificial, as well as in the natural amorphous silica, varies within very considerable limits, whilst the water can be partially driven off at low temperatures, so that it is now supposed not to be chemically combined.

THE SILICATES.

517 Although no solid hydrate of silicic acid possessing a constant composition is known, we are acquainted with an extremely large number of the salts of silicic acid termed *silicates*, of which by far the largest proportion occur in nature as distinct mineral species. Of great theoretical interest also are the volatile organic silicates or silicic ethers, which correspond in formula with the hypothetical modifications of silicic acid, the

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[1] Butzureanu, *Ann. Sci. Univ. Jassy.*, 1901, **1**, 319.

hydrogen atoms of the latter being replaced by monovalent organic radicals. Our knowledge of the chemical nature of the mineral silicates is very limited, and does not, as a rule, extend beyond the empirical or simplest formula of the compound, and all attempts to classify them are, therefore, of a somewhat speculative nature.

Evidences of the chemical structure of certain mineral silicates have, however, been obtained from the transformations which they undergo in nature, and from the alterations which may be brought about in the laboratory by the action of heat and other agents upon them; thus, for example, garnet, $Al_2(SiO_4)_3Ca_3$, when fused yields anorthite, $Al_6(SiO_4)_6Ca_3$, and a calcium silicate.

Many silicates have been prepared artificially either by the fusion of the constituents in the proper proportions with or without a flux, or by heating them together with water at a high temperature under pressure. Thus felspar, mica, olivine, garnet and others have all been prepared artificially, and these researches have thrown much light on the study of minerals and of the igneous rocks in which these minerals occur.[1]

A number of the naturally occurring silicates contain water, which may be either present as water of crystallisation, which is lost at a comparatively low temperature, or as water of constitution, in which case it is only lost on strong ignition.

According to Clarke,[2] all the silicates may be classed as salts of five silicic acids, a few examples of each class being given in the following table.

Besides normal salts there are double and triple salts, and acid and basic salts.

The small Roman numerals placed over the symbols denote the number of atoms of hydrogen replaced by the metal or group in question. In many minerals some of the metals are partially displaced by equivalent amounts of other isomorphous elements.

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[1] For further information on this point see Fuchs, *Die künstlichen Mineralien* (Harlem, 1870). Fouqué and Lévy, *Synthèse des Minéraux et des Roches* (Paris, 1882). Bourgeois, *Reproduction artificielle des Minéraux* (Paris, 1884). Traube, *Ber.*, 1893, **26**, 2735.

[2] Clarke, *Bull. U. S. Geol. Survey*, 1895, *No.* 125, **1**, see also Groth, *Tabellarische Uebersicht der Mineralien* (*Vienna*, 1882).

I. Derivatives of orthosilicic acid, H_4SiO_4 or $Si(OH)_4$.

Ethyl orthosilicate . . .	$(C_2H_5)_4SiO_4$.
Sodium silicate	Na_4SiO_4.
Eulytite	$\overset{iii}{Bi}_4(SiO_4)_3$.
Nephelite	$\overset{iii}{Al}_3(SiO_4)_3\overset{i}{Na}_3$.
Muscovite (potash mica) .	$\overset{iii}{Al}_3(SiO_4)_3\overset{i}{K}H_2$.
Andalusite	$\overset{iii}{Al}_3(SiO_4)_3(\overset{i}{AlO})_3$.
Topaz	$\overset{iii}{Al}_3(SiO_4)_3(\overset{i}{AlF_2})_3$.
Anorthite	$\overset{iii}{Al}_6(SiO_4)_6\overset{ii}{Ca}_3$.
Thomsonite	$\overset{iii}{Al}_6(SiO_4)_6\overset{ii}{Ca}_3\ 7H_2O$.
Natrolite	$\overset{iii}{Al}_2(SiO_4)_3\overset{i}{Na}_2H_4$.
Common garnet	$\overset{iii}{Al}_2(SiO_4)_3\overset{ii}{Ca}_3$.
Phenakite	$\overset{ii}{Be}_2SiO_4$.
Zircon	$\overset{iv}{Zr}SiO_4$.

II. Derivatives of metasilicic acid, H_2SiO_3 or $OSi(OH)_2$ $[Si(OH)_4-H_2O]$.

Ethyl metasilicate . . .	$(\overset{i}{C_2H_5})_2SiO_3$.
Potassium metasilicate .	K_2SiO_3.
Wollastonite	$\overset{ii}{Ca}_3(SiO_3)_3$.
Pectolite	$\overset{ii}{Ca}_2(SiO_3)_3NaH$.
Beryl	$\overset{iii}{Al}_2\overset{ii}{Be}_3(SiO_3)_6$.

III. Derivatives of diorthosilicic acid, $H_6Si_2O_7$ $[2Si(OH)_4-H_2O]$.

Barysilite	$\overset{ii}{Pb}_3(Si_2O_7)$.
Apophyllite	$\overset{ii}{Ca}_2(Si_2O_7)_3H_{12}(\overset{i}{CaOH})_2$.

IV. Derivatives of dimetasilicic acid, $H_2Si_2O_5$ $[2OSi(OH)_2-H_2O]$.

Petalite	$\overset{iii}{Al}(Si_2O_5)_2\overset{i}{Li}$.
Millarite	$\overset{iii}{Al}_2(Si_2O_5)_6HK\overset{ii}{Ca}_2$.

V. Derivatives of trisilicic acid, $H_4Si_3O_8$ $[3Si(OH)_4 - 4H_2O]$.

Albite	$\overset{iii}{Al}_3(Si_3O_8)_3Na_3$.
Orthoclase	$\overset{iii}{Al}_3(Si_3O_8)_3K_3$.
Stilbite	$\overset{iii}{Al}_6(Si_3O_8)_6\overset{ii}{Ca}_3,18H_2O$.

The silicates of the alkali-metals are the only ones soluble in water. These form the so-called soluble glass, which dissolves the more readily the larger the quantity of alkali it contains. Van Helmont was acquainted with this property of the silicates, and was aware that acids precipitated silicic acid from such an alkaline solution.

Of the silicates insoluble in water, some, and especially those which are hydrated silicates containing water in combination, are easily attacked by hydrochloric acid. In this case the silicic acid separates out as a gelatinous mass.

In order to decompose the silicates which are unattacked by acids, it is necessary to fuse them with an alkali carbonate and afterwards to decompose the fused mass with hydrochloric acid.

518 By the action of cold water on certain compounds of silicon with the halogens, other oxyacids of silicon are formed, which are analogous to certain organic acids in their constitutions, and have been named after these acids.

Silico-formic anhydride, $Si_2H_2O_3$ or $(HSiO)_2O$, is obtained by the action of cold water on silico-chloroform or iodoform :—[1]

$$2SiHCl_3 + 3H_2O = 6HCl + Si_2H_2O_3.$$

It is an insoluble white powder, is very unstable, and is decomposed by dilute ammonia giving silicic acid and hydrogen.

Silico-oxalic acid, $H_2Si_2O_4$ or $(SiOOH{\cdot}SiOOH)_n$.—Silicon trichloride or tri-iodide is decomposed by ice-cold water with formation of this body,[2] which is an insoluble white powder, and is decomposed by weak bases with evolution of hydrogen and formation of a silicate :—

$$H_2Si_2O_4 + 4KOH = 2K_2SiO_3 + 2H_2O + H_2.$$

When heated or rubbed it decomposes with a feeble explosion.

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[1] Friedel and Ladenburg, *Annalen*, 1880, **203**, 250.

[2] Friedel and Ladenburg, *Annalen*, 1880, **203**, 250; Gattermann and Weinlig, *Ber.*, 1894, **27**, 1943.

Silico-mesoxalic acid, $Si_3H_4O_6$ or $(SiOOH \cdot Si(OH)_2 \cdot SiOOH)_n$, is formed when silicon octochloride is allowed to stand in moist air at 0°. Like the preceding bodies it is an unstable white powder, and is decomposed by hot water into silicic acid and hydrogen.[1]

SILICON OXYCHLORIDE, Si_2Cl_6O.

519 When the vapour of silicon tetrachloride is passed over felspar, $Al_3K_3(Si_3O_8)_3$, heated to whiteness in a porcelain tube, potassium chloride and silicon oxychloride are formed, and this compound is also obtained when a heated mixture of chlorine with one-fifth to one half of its volume of oxygen is passed over crystalline silicon at about 800°.[2] It is a colourless fuming liquid boiling at 137°, and is easily decomposed by water into silicic and hydrochloric acids. Its vapour density is 10·05, corresponding with the formula given. By the further action of this oxychloride on heated felspar, or, better, by repeatedly passing a mixture of oxygen and the oxychloride through a red-hot tube filled with pieces of porcelain, the following series of oxychlorides was obtained by Troost and Hautefeuille:—[3]

	Boiling point.
$Si_4O_3Cl_{10}$	152° to 154°
$Si_4O_4Cl_8$	198° to 202°
$Si_8O_{10}Cl_{12}$	about 300°
$(Si_2O_3Cl_2)_n$	above 400°
$(Si_4O_7Cl_2)_n$	,, 440°.

The molecular weights of the first three have been ascertained by a determination of their vapour densities, whilst those of the last two compounds are unknown, but are doubtless multiples of the simplest ratio.

SILICON AND SULPHUR.

SILICON DISULPHIDE, SiS_2.

520 When the vapour of carbon bisulphide is led over a mixture of silica and carbon, such as is employed for the

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[1] Gattermann and Weinlig, *Ber.*, 1894, **27**, 1943; Gattermann and Ellery, *Ber.*, 1899, **32**, 1114.

[2] Troost and Hautefeuille, *Bull. Soc. Chim.*, 1881, [2], **35**, 360.

[3] *Ann. Chim. Phys.*, 1876, [5], **7**, 453.

preparation of the tetrachloride, and the mixture heated to whiteness, silicon disulphide is formed.

It may also be prepared by heating an intimate mixture of amorphous silicon and three times its weight of powdered sulphur in a crucible at 150°, and throwing the mass in successive small portions into a red-hot crucible, the product being obtained free from silicon and silica by sublimation under reduced pressure.[1]

It is also formed when lithium silicide is added to molten sulphur.[2]

Silicon disulphide crystallises in long white, silky needles, which burn in air to silica and sulphur dioxide, and are decomposed by water into hydrogen sulphide and silica.[3]

By melting sodium sulphide with silicon disulphide *sodium metathiosilicate*, Na_2SiS_3, is formed as a brownish-black mass, which evolves sulphuretted hydrogen on treatment with water, and reacts with chlorine with evolution of heat and formation of chlorides of sulphur and silicon.[4] Thio-silicates have been found along with other complex silicates in the lava of Vesuvius.

An orange-yellow coloured volatile *sub-sulphide*, SiS, and an *oxysulphide of silicon*, SiSO, are said to be formed by the action of sulphuretted hydrogen on silicon at a white heat.[5]

Silicon Chlorohydrosulphide, $SiCl_3SH$.—This compound was discovered by Pierre,[6] but its exact composition was determined by Friedel and Ladenburg.[7] In order to prepare it a mixture of sulphuretted hydrogen and the vapour of silicon tetrachloride is passed through a red-hot porcelain tube:—

$$SiCl_4 + H_2S = SiCl_3HS + HCl.$$

It is a colourless liquid which boils at 96°, and fumes in the air, water decomposing the compound into hydrochloric and silicic acids, sulphuretted hydrogen and sulphur. Its vapour possesses a specific gravity of 5·78.

Silicon thiochloride, $SiSCl_2$, is formed when the vapour of the chlorohydrosulphide is circulated through a glass tube

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[1] Hempel and Haasy, *Zeit. anorg. Chem.*, 1900, **23**, 32.

[2] Moissan, *Compt. Rend.*, 1902, **134**, 1083.

[3] Frémy, *Ann. Chim. Phys.*, 1853, [3], **38**, 314.

[4] Hempel and Haasy, *Zeit. anorg. Chem.*, 1900, **23**, 32.

[5] Colson, *Bull. Soc. Chim.*, 1882, [2], **38**, 56.

[6] *Ann. Chim. Phys.*, 1848, [3], **24**, 286.

[7] *Ann. Chim. Phys.*, 1872, [4], **27**, 416.

maintained at a temperature higher than that used in the preparation of the latter compound. It may be crystallised from carbon bisulphide in colourless prisms, melting at 75° and distilling at 92° under 22·5 mm. pressure, and is decomposed by distillation at ordinary pressures into silicon tetrachloride and silicon disulphide, whilst water decomposes it into hydrochloric and silicic acids, sulphuretted hydrogen and sulphur.[1]

Silicon thiobromide, $SiSBr_2$.—This body is obtained when a mixture of silicon tetrabromide and hydrogen sulphide is heated to 150° in the presence of aluminium bromide. It solidifies in large colourless plates melting at 93°, and boils without decomposition at 150° under 18·3 mm. pressure.[2]

SILICON AND NITROGEN.

521 When solutions of ammonia and silicon tetrachloride in benzene are allowed to react at a temperature below 0°, *silicon tetramide*, $Si(NH_2)_4$, and ammonium chloride are formed,[3] and the same substances are also obtained when liquid ammonia and liquid silicon tetrachloride are mixed together below 0° :—[4]

$$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl.$$

The ammonium chloride is dissolved out by treatment with liquid ammonia in which the tetramide is insoluble, the latter being left as an amorphous white body, which is very unstable and loses ammonia when heated above 0° forming *silicon di-imide*, $Si(NH)_2$, the decomposition being complete at 120°.

The last compound is also obtained by the action of liquid ammonia on silicon disulphide or silicon thiochloride.[5]

The white body obtained by Persoz[6] by action of gaseous ammonia on silicon tetrachloride, to which the formula $SiCl_4,6NH_3$ was given, is probably a mixture of silicon di-imide and ammonium chloride,[7] for Gattermann[8] obtained from it

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[1] Blix and Wirbelauer, *Ber.*, 1903, **36**, 4220.

[2] Blix, *Ber.*, 1903, **36**, 4218.

[3] Lengfield, *Amer. Chem. J.*, 1899, **21**, 531.

[4] Vigouroux and Hugot, *Compt. Rend.*, 1903, **136**, 1670.

[5] Blix and Wirbelauer, *Ber.*, 1903, **36**, 4220.

[6] *Annalen*, 1842, **44**, 319.

[7] Lengfield, *Amer. Chem. J.*, 1899, **21**, 531.

[8] Gattermann, *Ber.*, 1889, **22**, 1, 94 ; see also Deville and Wöhler, *Annalen* 857, **104**, 256.

a substance of the composition $Si(NH)_2$, whilst Blix and Wirbelauer[1] have prepared the di-imide from it in the pure state by treatment with liquid ammonia.

Silicon di-imide is an infusible, amorphous white powder; it is very stable and may be heated in vacuum without decomposition, whilst it forms with hydrochloric acid a white hydrochloride, $Si(NH)_2,2HCl$ (Blix and Wirbelauer).

Both the tetramide and di-imide are decomposed by water giving silica and ammonia; the di-imide when heated to 900° in an atmosphere of nitrogen, loses ammonia and forms *silicon nitrimide* (*silicam*),[2] Si_2N_3H, a body which was first obtained by Schützenberger and Colson[3] by igniting the product of the action of ammonia on silicon tetrachloride in ammonia gas.

Silicon nitrimide is an amorphous powder unacted on by water, which, on heating to 1200°—1300°, loses more ammonia, and yields silicon nitride, Si_3N_4.

Silicon nitride.—When silicon is strongly heated in nitrogen gas, a white amorphous substance, known as silicon nitride, is produced. If pure nitrogen is employed, the nitride formed has, according to Schützenberger,[4] the composition Si_2N_3, and is insoluble in hydrofluoric acid. When the experiment is carried out, as it was by Deville and Wöhler,[5] by heating silicon in a crucible placed inside another, which was packed with carbon to prevent as far as possible the access of oxygen, the product contains silicon carbonitride, Si_2C_2N, silicon carbide, SiC, silicon carboxide, SiCO, and a nitride of the formula Si_3N_4 which dissolves in hydrofluoric acid with formation of ammonium silicofluoride.[6]

Silicon thiodiamide (*silico-thiourea*), $SiS(NH_2)_2$, is formed along with ammonium chloride when dry ammonia is passed through a benzene solution of silicon thiobromide. When the ammonium bromide is removed by washing with liquid ammonia, the silicon thiodiamide is left as a colourless amorphous powder, which forms salts with halogen acids, and is decomposed by water into silica, ammonia and sulphuretted hydrogen.[7]

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[1] *Ber.*, 1903, **36**, 4220.

[2] Blix and Wirbelauer, *Ber.*, 1903, **36**, 4220.

[3] *Compt. Rend.*, 1881, **92**, 1511.

[4] *Compt. Rend.*, 1879, **89**, 644; 1881, **92**, 1508.

[5] *Annalen*, 1859, **110**, 248.

[6] *Compt. Rend.*, 1892, **114**, 1089.

[7] Blix, *Ber.*, 1903, **36**, 4218.

SILICON AND BORON.

522 Two borides of silicon have been prepared by Moissan and Stock[1] by heating one part of boron with five parts of crystalline silicon to a very high temperature in a vessel of refractory clay, by means of an alternating current. The cooled mass was treated with a cold mixture of hydrofluoric and nitric acids, washed with hot water, dried, and heated in a silver crucible with moist caustic potash, care being taken that the temperature did not rise above the fusion point of the potash, the crystals left being washed alternately with hot water and nitric acid and dried at 130°. In this way a mixture of *silicon triboride*, SiB_3, and *silicon hexaboride*, SiB_6, was obtained.

By boiling this mixture with nitric acid the hexaboride is oxidised and the triboride, which is only very slowly acted on, is obtained in black rhombic plates, having a density of 2·52; whilst by treatment at a high temperature with fused anhydrous potash the triboride is decomposed and the hexaboride left in thick black opaque crystals with a density of 2·47, which are intermediate between ruby and diamond in hardness and conduct electricity.

Both borides are soluble in molten silicon, and are attacked by fluorine when gently heated, and by chlorine and bromine at higher temperatures.

SILICON AND CARBON.

SILICON CARBIDE, SiC.

523 Silicon carbide is formed when a mixture of coke, sand and salt is fused in an electric furnace employing carbon terminals,[2] and may be obtained pure by fusing silicon with the requisite amount of carbon in the electric furnace.[3] It is also formed by the action of carbon on iron or calcium silicide, by fusing calcium carbide with silica in the electric furnace,[4] and by the union of the vapours of carbon and silicon in the electric furnace, needles of the carbide being deposited (Moissan).

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[1] *Compt. Rend.*, 1900, **131**, 139.

[2] Mühlhäuser, *Zeit. anorg. Chem.*, 1893, **5**, 105.

[3] Moissan, *Compt. Rend.*, 1893, **117**, 425.

[4] Moissan, *Compt. Rend.*, 1897, **124**, 839.

The crystals are colourless or sapphire blue and are usually found as six-sided plates, but when formed by the combination of the two vapours they are prismatic. Their specific gravity is 3·12 and they are hard enough to scratch rubies. Silicon carbide is not oxidised by oxygen at 1,000° and is not attacked by sulphur vapour, by fused potassium nitrate, or by any acid. It is completely decomposed by chlorine at 1,200°, and on fusion with lead chromate it is gradually oxidised, whilst fused caustic potash slowly converts it into potassium carbonate and silicate.

The crude material, obtained by the method first described, is known as *carborundum* and is used as a cutting and polishing agent. It is manufactured in large quantities at Niagara Falls.

SILICON CARBOXIDE, $SiCO$.

524 When silicon is heated to whiteness in an atmosphere of carbon dioxide, a greenish white mass is left, which after treatment with hydrofluoric acid has the composition $(SiCO)_x$.

$$3Si + 2CO_2 = SiO_2 + 2SiCO.$$

This compound is not acted on by alkalis and is not affected by being heated in oxygen, but is oxidised by a mixture of oxide and chromate of lead. At a lower temperature silicon carbide is formed.

Amorphous substances of the empirical formulæ, $SiCO_3$, Si_2C_2O, and $Si_2C_3O_2$ have also been obtained by analogous methods.[1]

CONSTITUTION OF THE VOLATILE SILICON COMPOUNDS.

525 Silicon forms a series of compounds which are volatile, and the molecular weights of which can, therefore, be readily ascertained. When this has been determined, it appears that the chemical constitution of these bodies, that is to say, the mode in which the different atoms are arranged in the molecule, can be most simply expressed on the assumption that silicon is a tetravalent element. The following graphic formulæ,

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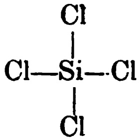
[1] Schützenberger and Colson, *Compt. Rend.*, 1881, **92**, 1508; 1892, **114**, 1087. Colson, *Bull. Soc. Chim.*, 1882, [2], **38**, 56.

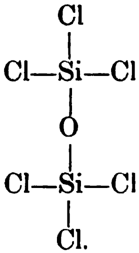
analogous to those of the carbon compounds, show the constitution of the most important of these compounds:—

Silicon tetrachloride,



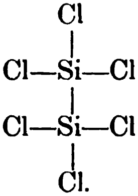
$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}Si{-}Cl}\\ |\\ \mathrm{Cl}\end{array}$$

Silicon oxychloride,



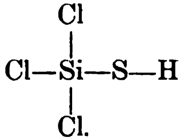
$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}Si{-}Cl}\\ |\\ \mathrm{O}\\ |\\ \mathrm{Cl{-}Si{-}Cl}\\ |\\ \mathrm{Cl.}\end{array}$$

Silicon trichloride,



$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{Cl{-}Si{-}Cl}\\ |\\ \mathrm{Cl{-}Si{-}Cl}\\ |\\ \mathrm{Cl.}\end{array}$$

Silicon chlorhydrosulphide,



$$\begin{array}{l}\quad\mathrm{Cl}\\ \quad\,|\\ \mathrm{Cl{-}Si{-}S{-}H}\\ \quad\,|\\ \quad\mathrm{Cl.}\end{array}$$

THE GASES OF THE HELIUM GROUP.

526 In his celebrated research on the action of the electric spark on air, published in the *Philosophical Transactions* for 1785, Cavendish describes an experiment in which he added excess of oxygen to a given volume of air and passed electric sparks through the mixture, collected over caustic potash, until no further diminution of bulk took place; he then absorbed the excess of oxygen by "liver of sulphur," "after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$th of the bulk of the phlogisticated air (nitrogen) let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole."

A century elapsed before the true explanation of the existence of this small proportion of unabsorbable gas was given, viz., the presence of a whole series of constituents of the atmosphere hitherto overlooked. No less than five distinct new gases have now been isolated from the air, and these have received the names Argon (ἄργον, idle, inactive), Neon (νέον, new), Helium (ἥλιος, the sun), Krypton (κρυπτὸν, hidden), Xenon (ξένος, stranger). Argon is present in by far the largest amount, and the others follow in the order given. The volume of these gases contained in the air amounts to $\frac{1}{84}$th part of that of the atmospheric nitrogen (or exactly 1·186 per cent.), and the history of their discovery is interesting as having been arrived at by exact physical measurements. It has already been stated (p. 124) that Lord Rayleigh determined with great care the weight of the litre of oxygen, hydrogen, and nitrogen. In the case of both oxygen and nitrogen, Rayleigh prepared each gas by different methods. Samples of oxygen obtained by electrolysis, by heating potassium chlorate, and by heating potassium permanganate, proved to possess the same weight. In order to ascertain whether nitrogen was also homogeneous, Rayleigh weighed nitrogen prepared from ammonia, and found that it was lighter than atmospheric nitrogen by about one-half per cent. This amount was far above the possible experimental error, and pointed to a distinct difference between the gases obtained from the two sources. What that difference might be was at first not clear, and many possible explanations were put forward. In 1894, Ramsay associated himself with

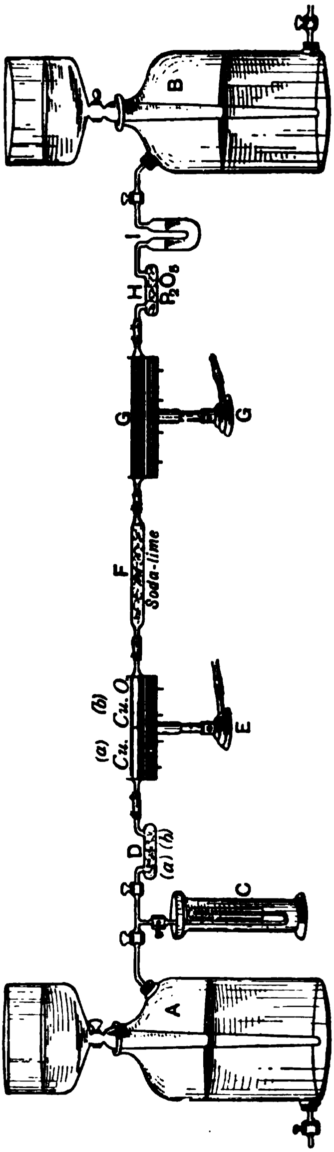


FIG. 216.

Rayleigh, and they proved that the above difference was due to the presence in the atmosphere of an inert gas heavier than nitrogen.[1] In order to collect this inert gas from the air two methods may be employed: (1) to pass atmospheric nitrogen over red-hot turnings of magnesium, which absorbs nitrogen forming a nitride; (2) to "spark" the gas with excess of oxygen in presence of caustic alkali. The apparatus used for the first of these is shown in Fig. 216. Atmospheric nitrogen is passed from gasholder (A) to gasholder (B) through a tube (G) filled with magnesium heated to redness to absorb nitrogen, over red-hot copper oxide (*a*, *b*), so as to ensure that any carbonaceous matter shall be burnt to carbon dioxide and water, and any hydrogen liberated by the treatment with magnesium at the same time burnt to water, the products being absorbed by soda lime placed in (F) and (I) and by phosphorus pentoxide in (D) and (H). After passing the gas backwards and forwards for about seven days, the volume of the original nitrogen was reduced to $\frac{1}{80}$th, and the density of the gas was 16·1, whilst a second treatment with fresh magnesium further reduced the volume and increased the density to 19·94.

The second method is an improvement on Cavendish's original experiment by which the nitrogen is electrically oxidised and absorbed by alkali as a mixture of nitrite and nitrate. One form of the apparatus which may be employed is shown in Fig. 217. Atmospheric nitrogen is passed from one gasholder to another (not shown in the figure) through a large glass balloon containing two copper electrodes with thick platinum terminals and tubes for supplying a constant stream of caustic soda solution. This latter serves to keep the surface of the globe cool and to absorb the nitrous fumes formed by the action of the electric arc, obtained by a powerful alternating current, on the mixture of oxygen and nitrogen.

The discovery of argon was soon followed by that of helium. In the year 1868, Lockyer observed in the spectrum of the solar chromosphere a line in the yellow nearly coincident with the double line of sodium, which he denoted as D_3, the wave length of which is 5,875. No terrestrial substance was known containing a corresponding line in its spectrum, and Lockyer and Frankland supposed that this line was due to the presence in the sun of an element which had not been discovered in

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[1] *Phil. Trans.* 1895, 187.

terrestrial matter, and they therefore proposed for it the name helium (ἥλιος, the sun). In 1889, Hillebrand[1] examined the action of dilute sulphuric acid on the mineral uraninite, which consists essentially of a uranate of uranyl and lead, containing rare earths, and obtained a gas which he found to have the usual properties of nitrogen, and proved that this gas was actually present. After the discovery of argon, Ramsay,[2] at the suggestion of Miers, examined the gas from the mineral cleveite, which is a variety of uraninite, thinking that this might contain argon. The result of his investigation showed that the gas from this mineral contained very little, if any, nitrogen; the spectrum showed that a small quantity of argon was present, but in addition other bright lines were noticed which did not occur in the argon spectrum. The most prominent of these was a line in the yellow which appeared to correspond with the line D_3 in the chromospheric spectrum, and this conclusion was confirmed by the exact measurements of Crookes. Helium was then prepared from a number of different minerals, and was found to be a chemically inert gas, like argon, but of density 1·98.

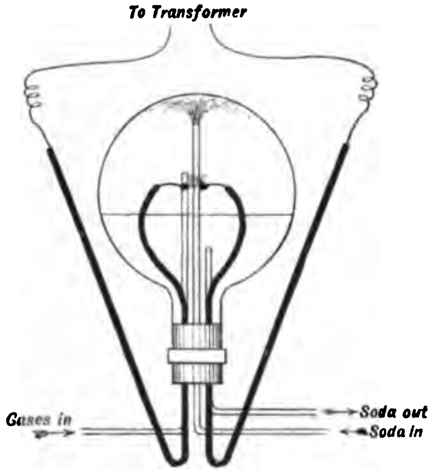

Fig. 217.

The characteristic line of helium was remarked in the

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[1] *Bull. U.S. Geol. Survey*, 1889, **78**, 43.

[2] *Journ. Chem. Soc.* 1895, 1107.

spectrum of the air by Kayser,[1] and the gas was subsequently isolated by Ramsay and Travers from atmospheric argon.

All attempts to obtain chemical compounds between helium and argon and other elements entirely failed, and hence it was necessary to fall back on physical methods for the determination of their atomic weights. The only method available for this purpose is that which depends on the determination of the number of atoms in the molecule from the ratio of the two specific heats of the gas, this value being itself calculated from the velocity of sound in the gas, as described on p. 129. The result of this was in both cases that the ratio of the two specific heats is 1 to 1·66, and therefore both gases must be regarded as monatomic. It hence follows from the known densities of the gases that the atomic weight of helium is 4, and that of argon 39·6.

The existence of these two gases of similar properties, and possessing atomic weights 4 and 39·6, led to the surmise that other analogous elements would also be found, and in particular one of intermediate atomic weight (about 20), which would thus complete a triad of elements similar in their atomic weight relations to many of the well known triads, such as nitrogen, phosphorus, and vanadium.[2]

The discovery of this missing gas was, after many failures, finally effected by the careful fractional distillation of the crude argon obtained directly from the atmosphere by the methods already described, and liquefied by means of liquid air boiling under reduced pressure. The gas first evolved by the evaporation of the liquid argon under these circumstances has the density 14, and by repeated condensation and fractional distillation, first at the temperature of liquid air boiling under diminished pressure, and then at that of boiling liquid hydrogen, can be resolved into helium, a new gas termed neon, of density 10, and argon.[3]

The fractional evaporation of a large volume of liquid air itself led to the further discovery of two new gases also belonging to this group.[4] The last portions of gas evolved possess,

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[1] *Chem. News*, August 23rd, 1895.

[2] Ramsay, *British Assor. Rep.*, 1897, 595 ; *Nature*, 1897, **56**, 378.

[3] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **63**, 438 ; *Phil. Trans.*, 1901, 47.

[4] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **63**, 405 ; *British. Assoc. Rep.*, 1898, 828. A full account of the discovery of all these gases and of their properties is to be found in Travers' "The Experimental Study of Gases" (Macmillan & Co. London, 1901).

after the removal of oxygen and nitrogen, a density of about 22, and by repeated fractionation yield argon, and two new gases, krypton, of density 41, and xenon, of density 64.

These three new gases all resemble argon and helium in their inert character, and in the fact that the ratio of their specific heats is 1 to 1·66, so that they have the atomic weights, neon = 19·9, krypton = 81·2, and xenon = 127.

The separation of these five new gases from all other known gases is effected by the methods already described. The only practical method for their separation from each other consists in fractional condensation and distillation at low temperatures.

HELIUM, He = 4 (H = 1).

527 Helium, as already mentioned, occurs in a considerable number of minerals, although in most cases the quantity present is small. Most of the minerals which yield the gas contain uranium, and the few in which uranium is not present contain yttrium or thorium. The three minerals which yield helium in the largest quantity are cleveite, the analogous bröggerite, and the uraninite first examined by Hillebrand. The gas obtained from the last of these contains at least 10 per cent. of nitrogen, which accounts for the results obtained in his original investigation. Helium has also been found, together in one case with argon, in the gases evolved from certain specimens of meteoric iron, whilst others give neither of these elements, and it has also been found in the gases from a number of mineral springs, such as those of King's well Bath, of Cauterets in the Pyrenees, and of Wildbad. Helium also occurs in the air to the extent of about 1—2 volumes in 1,000,000 volumes.

In order to prepare helium, one of the above minerals is finely powdered and heated in an evacuated tube, either alone or with an equal weight of acid potassium sulphate, or with dilute sulphuric acid, the gas evolved being collected over mercury.[1] Any admixed gases, such as hydrogen, oxygen, carbon dioxide, or hydrocarbons, may be removed in the usual manner, and nitrogen by magnesium as described above. Argon cannot be removed by chemical means, but may be separated by diffusion, or more readily by cooling with liquid hydrogen.

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[1] Travers, *Proc. Roy. Soc.*, 1898, **64**, 131; *Journ. Chem Soc.*, 1895, 685.

Helium has also been obtained in considerable quantities from the gases evolved from the King's well Bath, which contain as much as 0·12 per cent. of helium by volume,[1] together with some argon; it is estimated that about 1,000 litres of helium are produced annually by this well.

528 *Properties of Helium.*—Like all the gases of this group, helium is remarkable for its inert behaviour, all attempts to cause it to enter into chemical combination having hitherto been without success. It is, however, absorbed by the platinum which is deposited on the walls of a vacuum tube containing platinum electrodes by the continued passage of the electric discharge, and is again evolved when the tube is heated. Since argon is only absorbed to a very slight extent under these circumstances, small amounts of helium can be separated from argon in this way.[2]

Helium is the only gas which has not yet been liquefied and shows no signs of liquefaction when exposed to the absolute temperature of 13° (−260 C.) and a pressure of 60 atmospheres.[3] It seems probable from the other properties of the gas that its critical temperature is below 9° Absolute (−264° C.), and its boiling point about 5° Absolute (−268° C.).[4]

On account of this extreme volatility the presence of helium can readily be demonstrated in a comparatively small volume of air. This may be effected either by cooling a tube containing about 50 cc. of air in liquid hydrogen, when both helium and neon can be detected spectroscopically in the residual gas,[5] or by cooling air to the temperature of liquid air in presence of wood charcoal, when hydrogen, helium, and neon can all be detected in the unabsorbed gas[6] (see p. 744).

Helium has the density 1·98 and is monatomic, so that its atomic weight is about 3·96; the refractivity of the gas is 0·1238 (air = 1).[7]

Helium is even less soluble than hydrogen in water, its coefficient of solubility being 0·01487 at 0·5° and 0·01371 at 25°.[8] It behaves like hydrogen on compression, the product

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[1] Rayleigh, *Proc. Roy. Soc.*, 1896, **59**, 198.

[2] Travers, *Proc. Roy. Soc.*, 1897, **60**, 449.

[3] Travers, Senter, and Jaquerod, *Proc. Roy. Soc.*, 1902, **70**, 484.

[4] Dewar, *Proc. Roy. Soc.*, 1901, **68**, 360.

[5] Dewar, *Proc. Roy. Soc.*, 1899, **64**, 231.

[6] Dewar, *Proc. Roy. Soc.*, 1904, **74**, 127.

[7] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 331.

[8] Estreicher, *Zeit. physikal. Chem.*, 1899, **31**, 176.

of pressure and volume increasing steadily with the pressure. On account of its low critical temperature it has been much employed in thermometry at low temperatures. Unlike hydrogen, it does not pass through heated platinum or palladium, but, like hydrogen, it diffuses through heated quartz, the amount of diffusion being distinct at 510° and very marked at 1,108°.[1]

The spectrum of helium is very characteristic; in addition to the yellow line D_3 (which, with instruments giving a wide dispersion, is found to be a double line), about seven other bright lines occur. The colour of the glow produced in a Plücker's tube containing pure helium varies with the pressure of the gas, being yellow when the pressure is about 7 mm., and green when it is only about 1–2 mm. This behaviour, together with the character of the spectrum, led Runge and Paschen[2] to the conclusion that helium consisted of two components, but this view has not been confirmed by experiment, all attempts to separate the gas into two different constituents by diffusion or other means having been unsuccessful.[3]

Production of Helium from Radium.—In 1903 Ramsay and Soddy observed the remarkable fact that the gas evolved from a solution of radium bromide in water contains helium.[4] Radium bromide is the bromide of a metallic element which was discovered in pitchblende by M. and Madame Curie[5] in 1898. It has the atomic weight 223·3, and in its chemical properties closely resembles barium. This substance is characterised by the remarkable property of *radioactivity*, which extends to all its salts. This phenomenon will be more fully discussed in Vol. II., but it may here be briefly described as the property of constantly emitting radiations which are possessed of energy. In the case of radium bromide the radiation has been analysed into no less than three different kinds of ray, and in addition to these so much heat is evolved that a mass of radium bromide maintains itself permanently at a temperature higher by 1°·5 C. than that of the surrounding objects.[6] Accompanying this extraordinary evolution of energy a gaseous substance, first known as "the emanation of radium,"

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[1] Jaquerod and Perrot, *Compt. Rend.*, 1904, **139**, 789.

[2] *Nature*, 1895, **52**, 520. [3] *Nature*, 1897, **56**, 380.

[4] *Proc. Roy. Soc.*, 1903, **72**, 204.

[5] *Compt. Rend.*, 1898, **127**, 1215.

[6] Curie and Laborde, *Compt. Rend.*, 1903, **136**, 673.

but now termed Exradio, is evolved in extremely small quantity. This substance can be condensed by exposure to low temperatures, and can be manipulated in all respects as a gas. Like the original radium bromide, it is itself radioactive, but slowly loses this property. When this substance is sealed up in a tube it at first gives a characteristic spectrum of its own, but after four days, the spectrum changes to that of helium, and the radioactive properties are found to have disappeared.[1] At the same time a considerable increase in volume occurs, the final volume being about three and a half times that of the original emanation. This remarkable transformation has been confirmed by several independent observers, and appears to be well established.[2] It is at present (1905) considered by many workers that a constant disintegration of the radium atom is in progress, which takes place with the evolution of an enormous amount of energy amounting to 10^9 calories per gram. This disintegration occurs in stages, yielding a series of substances of decreasing atomic weight and diminished potential energy. Of these disintegration products the emanation is the first, whilst helium is the only final product which has hitherto been recognised. This remarkable production of helium from radium accounts for the presence of small amounts of this element in minerals which contain radioactive substances. In this connection it is also of interest that the deposits from the Buxton hot springs and the King's well Bath, have been found by Strutt[3] to contain traces of a radioactive element, so that the occurrence of helium in the latter well is probably due to some similar process of disintegration.

These observations, which open up a new field of research of surpassing interest, suggest that the other inert or noble gases, as they have been termed from analogy with the noble metals, may be derived from a similar source. No experimental support has, however, been so far obtained for this idea.

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[1] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 206; 1904, **73**, 346.

[2] Dewar and Curie, *Compt. Rend.*, 1904, **138**, 190. Indrikson, *Physikal. Zeitschr.*, 1904, **5**, 214. Himstedt and Meyer, *Ann. Physik.*, 1904, (4), **15**, 184.

[3] *Proc. Roy. Soc.*, 1904, **73**, 191.

NEON, Ne = 19·9 (H = 1).
= 20 (O = 16).

529 Neon occurs in the air to the extent of about 1–2 parts per 100,000 (Ramsay and Travers), and has also been found along with helium in the gas from the King's well Bath.[1] It is isolated from the more volatile portion of the crude argon obtained from the air, by fractional condensation and evaporation at the temperature of boiling hydrogen. The physical properties of the gas are not accurately known, but the critical temperature of the gas lies below 63° Absolute (−210° C.) and its boiling point at about 30°–40° Absolute (−243° to −233° C.), so that next to helium and hydrogen, neon is the least easily condensable gas known; at the temperature of boiling liquid hydrogen it appears to solidify (Ramsay and Travers).[2] The gas has the density 9·95 (H = 1), and therefore, since it is monatomic, the atomic weight is 19·9. The refractivity of the gas is 0·2345 (air = 1).[3] The spectrum of the gas contains a large number of lines in the red and green, and is not materially altered when a spark gap and Leyden jar are introduced into the circuit. When exposed to the electric discharge in a vacuum tube the gas gives a reddish orange glow.[4]

ARGON, A = 39·6 (H = 1).
= 39·9 (O = 16).

530 Argon is by far the most abundant of the inert gases of the atmosphere, forming as it does about 1·3 per cent. of the air by weight[5] and 0·933 per cent. by volume.[6] Hence it amounts to 1·186 per cent. of "atmospheric nitrogen." It occurs in a very large number of mineral waters and springs, and has been found in the volcanic gases of Mt. Pelée, in which it is present in a somewhat higher proportion to the nitrogen than in air.[7]

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[1] Dewar, *Proc. Roy. Soc.*, 1904, **74**, 127.

[2] See also Dewar, *Proc. Roy. Soc.*, 1901, **68**, 360.

[3] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 331.

[4] Baly, *Proc. Roy. Soc.*, 1903, **72**, 84; *Phil. Trans.*, 1904, A, **202**, 183.

[5] Leduc, *Compt. Rend.*, 1896, **123**, 805.

[6] Moissan, *Compt. Rend.*, 1903, **137**, 600.

[7] Moissan, *Compt. Rend.*, 1902, **135**, 1085.

Argon has also been found, together with helium, in the gas evolved on heating numerous minerals, and also from one specimen of meteoric iron.

It is isolated from the air by the methods already described[1] (p. 907), but it is now usual to replace the magnesium by a strongly ignited mixture of magnesium and lime, which contains metallic calcium, and to remove the last traces of nitrogen by passing the gas over heated calcium.[2]

In order to obtain it quite pure, the crude gas is submitted to fractional condensation and evaporation. The actual proportion of the other inert gases present in crude atmospheric argon is, however, very small, and does not exceed about 0·25 per cent., nearly 85 per cent. of this impurity being neon.

Argon has been condensed to a colourless liquid which boils at 86°·9 Absolute (−186°·1 C.), at which temperature its density is 1·4046,[3] and solidifies only a few degrees below its boiling point at 83°·4 Absolute (−189°·6 C.). Its critical temperature is 155°·6 Absolute (−117°·4 C), and the critical pressure 52·9 atmospheres (Ramsay and Travers).

Argon is considerably more soluble in water than nitrogen, its coefficient of solubility[4] being 0·05612 at 1° and 0·02567 at 50°; hence in the gases expelled from water saturated with air the ratio of argon to nitrogen is higher than in the atmosphere. The gas has the refractivity[5] 0·9655 (air = 1); it passes through rubber more quickly than nitrogen[6] or carbon dioxide[7] and does not pass through heated platinum or palladium. Its rate of effusion is about 5 per cent. less than would be expected from its molecular weight.[8]

Pure argon has the density 19·83 (H = 1) or 19·955 (O = 16), and one litre of the gas under normal conditions weighs 1·7828 grams. As the gas has been shown to be monatomic it follows that its atomic weight is 39·6 (H = 1).

All attempts to combine argon with other elements have hitherto failed. As has been stated, it does not combine with oxygen under the influence of the electric discharge, nor with

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[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **64**, 183.

[2] Moissan and Rigaut, *Compt. Rend.*, 1903, **137**, 773.

[3] Baly and Donnan, *Journ. Chem. Soc.*, 1902, 914.

[4] Estreicher, *Zeit. physikal. Chem.*, 1899, **31**, 176.

[5] Ramsay and Travers, *Proc. Roy. Soc.*, 1899, **64**, 183.

[6] Rayleigh, *Phil. Mag.*, 1900, [5], **49**, 220.

[7] Kistiakowski, *J. Russ. Chem. Soc.*, 1898, **30**, 576.

[8] Donnan, *Phil. Mag.*, 1900, [5], **49**, 423.

metallic magnesium. No action is observed when argon is sparked with chlorine or with hydrogen. It is not absorbed or altered in volume when passed through a red-hot tube together with the vapours of phosphorus, sulphur, tellurium or sodium. Fused alkalis and alkali peroxides do not act upon it, nor does nascent chlorine. Fluorine, the most active of the elements, does not enter into combination with argon, and this gas suffers no diminution in volume when sparked with the vapour of carbon tetrachloride nor when passed over heated titanium and uranium.

Spectrum of Argon.—The spectrum of argon is extremely characteristic and has been carefully examined.[1]

Two different spectra are obtained according to the pressure of the gas and the intensity of the electric discharge; with a pressure of 3 mm. an orange glow is observed in the tube, and the spectrum shows a large number of lines in the red, two of which, having wave lengths of 6965·6 and 7056·4, are especially prominent. Bright lines are also observed in all parts of the spectrum, the most noticeable being the line 6038·4 in the yellow, five lines in the green, the two brightest having wave lengths of 5610 and 4702 respectively, and five in the violet, the brightest of which has a wave length of 4200. With a lower pressure of gas and a more intense discharge the tube shows a bluish glow and the spectrum consists of 119 lines.

KRYPTON, Kr = 81·2 (H = 1).
= 81·8 (O = 16).

531 Krypton occurs in the air to the extent of about 1 part in 1,000,000 by volume and is found in the less volatile portions of liquid air, from which it is obtained pure by repeated fractional evaporation after the removal of oxygen and nitrogen (Ramsay and Travers). It may also be separated from air, along with xenon, by passing the air through a spiral tube packed with glass wool and cooled by liquid air.[2]

It boils at 121°·3 Absolute (−151°·7 C.), at which temperature its density is 2·155, and has the critical temperature 210°·5

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[1] Crookes, *Phil., Trans.* 1895, 243; Kayser, *Chem. News.*, 1895, **72**, 99; Eder and Valenta, *Monatsh.*, 1895, **16**, 893; 1896, **17**, 50. Trowbridge and Richards, *Phil. Mag.*, 1897, [5], **43**, 77.

[2] Dewar, *Proc. Roy. Soc.*, 1901, **68**, 360.

Absolute (–72°·5 C.), and the critical pressure 54·3 atmospheres. The refractivity of the gas is 1·449 (air = 1).[1]

The density of krypton is 40·6 (H = 1) and it is monatomic, so that its atomic weight is 81·2.

With a discharge of low intensity the gas gives in a vacuum tube a yellowish-green glow, the spectrum of which contains conspicuous lines in the yellow and green, whilst with a more intense discharge the glow becomes blue and gives a very complex spectrum (Baly).[2]

XENON, X = 127 (H = 1).
= 128 (O = 16).

532 Xenon is at once the least volatile and the least abundant of the inert gases which are known to exist in the air, and is only present in the proportion of 1 part in 20,000,000 by volume (Ramsay and Travers). It boils at 163°·9 Absolute (–109°·1 C.), at which temperature its density is 3·52, and has the critical temperature 287°·8 Absolute (+14°·8 C.), and the critical pressure 57·2 atmospheres. It readily solidifies at the temperature of liquid air, and the solid volatilises at a higher temperature without melting. The refractivity of the gas is 2·364 (air = 1). The density of the gas is 63·5 (H = 1), so that its atomic weight is 127.

The spectrum, like that of argon and krypton, changes with the intensity of the discharge. With one of low intensity the glow of the tube is blue, the spectrum containing only faint lines in the red and green. When a spark gap and Leyden jar are introduced the glow becomes green, and a large number of green lines are present in the complex spectrum which is then seen (Baly).

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[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 331.

[2] See also Liveing and Dewar, *Proc. Roy. Soc.*, 1901, **68**, 389.

By Act of Parliament (27 *and* 28 *Vict. cap.* 117, 29*th July*, 1864) *the use of the* ***Metrical System of Weights and Measures*** *is rendered legal.*
The weight of the Kilogram is settled by this Act to be equal to 15432·3488 *English Grains.*

COMPARISON OF THE METRICAL WITH THE COMMON MEASURES. BY DR. WARREN DE LA RUE.

MEASURES OF LENGTH.

	In English Inches.	In English Feet =12 Inches.	In English Yards =3 Feet.	In English Fathoms =6 Feet.	In English Miles =1,760 Yards.
Millimeter	0·03937	0·0032809	0·0010936	0·0005468	0·0000006
Centimeter.	0·39371	0·0328090	0·0109363	0·0054682	0·0000062
Decimeter	3·93708	0·3280899	0·1093633	0·0546816	0·0000621
Meter	39·37079	3·2808992	1·0936331	0·5468165	0·0006214
Decameter	393·70790	32·8089920	10·9363310	5·4681655	0·0062138
Hectometer	3937·07900	328·0899200	109·3633100	54·6816550	0·0621382
Kilometer	39370·79000	3280·8992000	1093·6331000	546·8165500	0·6213824
Myriameter	393707·90000	32808·9920000	10936·3310000	5468·1655000	6·2138244

1 Inch = 2·539954 Centimeters.
1 Foot = 3·0479449 Decimeters.
1 Yard = 0·91438348 Meter.
1 Mile = 1·6093149 Kilometer.

MEASURES OF SURFACE.

	In English Square Feet.	In English Square Yards=9 Square Feet.	In English Poles =272·25 Square Feet.	In English Roods =10,890 Square Feet.	In English Acres =43,560 Square Feet.
Centiare or square meter	10·7642993	1·1960333	0·0395383	0·000988457	0·0002471143
Are or 100 square meters	1076·4299342	119·6033260	3·9538290	0·098845724	0·0247114310
Hectare or 10,000 square meters . .	107642·9934183	11960·3326020	395·3828959	9·884572398	2·4711430996

1 Square Inch = 6·4513669 Square Centimeters.
1 Square Foot = 9·2899683 Square Decimeters.
1 Square Yard = 0·83609715 Square Meter or Centiare.
1 Acre = 0·404671021 Hectare.

MEASURES OF CAPACITY.

	In Cubic Inches.	In Cubic Feet =1,728 Cubic Inches.	In Pints = 34·65923 Cubic Inches.	In Gallons = 8 Pints =277·27384 Cubic Inches.	In Bushels = 8 Gallons =2218·19075 Cubic Inches.
Milliliter, or cubic centimeter . . .	0·061027	0·0000353	0·001761	0·00022010	0·000027512
Centiliter, or 10 cubic centimeters .	0·610271	0·0003532	0·017608	0·00220097	0·000275121
Deciliter, or 100 cubic centimeters .	6·102705	0·0035317	0·176077	0·02200967	0·002751208
Liter, or cubic decimeter	61·027052	0·0353166	1·760773	0·22009668	0·027512085
Decaliter, or centistere	610·270515	0·3531658	17·607734	2·20096677	0·275120846
Hectoliter, or decistere	6102·705152	3·5316581	176·077341	22·00966767	2·751208459
Kiloliter, or stere, or cubic meter .	61027·051519	35·3165807	1760·773414	220·09667675	27·512084594
Myrialiter, or decastere	610270·515194	353·1658074	17607·734140	2200·96676750	275·120845937

1 Cubic Inch = 16·3861759 Cubic Centimeters. 1 Cubic Foot = 28·3153119 Cubic Decimeters.
1 Gallon = 4·543457969 Liters.

MEASURES OF WEIGHT.

	In English Grains.	In Troy Ounces =480 Grains.	In Avoirdupois Lbs. =7,000 Grains.	In Cwts. = 112 Lbs. =734,000 Grains.	Tons = 20 Cwt. = 15,620,000 Grains.
Milligram	0·015432	0·000032	0·0000022	0·00000002	0·000000001
Centigram	0·154323	0·000322	0·0000220	0·00000020	0·000000010
Decigram	1·543235	0·003215	0·0002205	0·00000197	0·000000098
Gram	15·432349	0·032151	0·0022046	0·00001968	0·000000984
Decagram	154·323488	0·321507	0·0220462	0·00019684	0·000009842
Hectogram	1543·234880	3·215073	0·2204621	0·00196841	0·000098421
Kilogram	15432·348800	32·150727	2·2046213	0·01968412	0·000984206
Myriagram	154323·488000	321·507267	22·0462126	0·19684118	0.009842059

1 Grain = 0·064798950 Gram. 1 Lb. Avd. = 0·45359265 Kilog.
1 Troy oz. = 31·103496 Gram. 1 Cwt. = 50·80237689 Kilog.

INDEX

THE END

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